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THEORETICAL
ELECTROCHEMISTRY

THEORETICAL ELECTROCHEMISTRY

BY

N. A. McKENNA, B.A. (OXON)

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1939

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TO
MY MOTHER

*who, by her sympathy and sacrifice,
gave me the courage and
the means to foster
my interest in science,
I dedicate this work
in gratitude.*

OXFORD 1935

LONDON 1938

PREFACE

THE theory of solutions has come increasingly in the last few years to imply the theory of electrically conducting solutions. This has been due largely to the success which has attended the application of electrostatics to ionic solutions made by Debye and Hückel in 1923. Since then the theory of interionic attraction has been extended to explain both the irreversible and the reversible (or free-energy) properties of dilute solutions of electrolytes and almost all the experimental work which has been carried out on dilute ionic solutions has confirmed the predictions of the theory. In the first part of this book an attempt has been made to emphasise the merits of this theory and to show how the properties of ionic solutions, considered in its light, fall into two well-defined groups, the irreversible properties requiring an application of the laws of hydrodynamics and the thermodynamic or reversible properties which are all closely bound up with the free-energy of the solution. A second section of the book is devoted to the thermodynamics of reversible cells and the theories of the galvanic cell. Particular attention has been given here to the kinetic interpretation of the E.M.F. set up in a cell since information about the mechanism of cell processes can only be obtained by such an approach. Finally, the properties of equilibria in solutions of electrolytes are discussed as a sub-section of the theory of solutions.

The book is not intended in any way to be comprehensive but I have tried to discuss the topics chosen as fully as is desirable or possible in so short a space and it is believed that sufficient detail has been given to show how recently-formulated theories of electrolytes and electrochemical processes have explained and correlated much of the body of fact which was, at one time, largely confusion.

I am indebted to the Clarendon Press for permission to

reproduce figures 3, 34, 35, 42, 60 and 62, to the President and Council of the American Chemical Society for allowing me to use figure 56 from their journal, and to the President and Council of the Royal Society and Professor Sidgwick for permission to copy figure 81 from the Proceedings of the Royal Society. My especial thanks are due to Mr. T. R. Parsons for his kind encouragement to me throughout the work and to Professor Hinshelwood and Mr. J. H. Wolfenden for their generous help on many points.

N. A. McKenna.

*Blackheath,
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December 1938.*

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TABLE OF SYMBOLS

A	= maximum work (first thermodynamic function).
B	= first Hückel coefficient in the expression for the activity coefficient.
D	= dielectric constant. second Hückel coefficient.
E	= electromotive force, electrode potential (arbitrary).
E°	= standard electrode potential.
$E_{\text{liq.}}$	= liquid junction potential.
F	= free energy (second thermodynamic function).
F	= the Faraday = 96,540 coulombs.
F°	= standard free energy.
$\bar{F}$	= partial molal free energy.
H	= heat content.
I	= ionization potential.
K	= equilibrium or dissociation constant.
K_a	= equilibrium constant expressed in activity terms.
K_c	= equilibrium constant expressed in concentration terms.
K_p	= equilibrium constant expressed in pressure terms.
K_w	= ionic product of water.
N	= Avogadro's number (number of molecules at N.T.P. of any gas contained in the gram molecular volume).
P	= pressure.
Q	= total energy, molecular heat content (Lewis).
R	= gas constant per gram molecule.
S	= entropy.
T	= temperature.
U	= total internal energy.
V	= volume.
V_c	= heat of dilution from concentration c to infinite dilution.
W	= work.
a	= activity; Debye-Hückel "ionic diameter."
c	= concentration.
e	= base of system of natural logarithms.

- e = electronic charge.
 f = activity coefficient.
 g_0 = osmotic coefficient = $\frac{\text{observed O.P.}}{\text{calculated O.P.}}$
 h = Planck's constant.
 i = van 't Hoff abnormality factor.
 j = Lewis factor defined as $1 - \frac{\theta}{\lambda_m}$ where θ is the lowering of the freezing point.
 k = Boltzmann's constant = $\frac{R}{N}$
 n_- = transport number of anion.
 n_+ = transport number of cation.
 n_i = number of ions of the species i .
 p = vapour pressure.
 u = mobility of anion.
 v = mobility of cation.
 $\left. \begin{matrix} u_\infty \\ v_\infty \end{matrix} \right\}$ = mobilities of anion and cation at infinite dilution.
 z_i = valency of an ion of the type i .
 α = Arrhenius degree of dissociation;
 first Onsager coefficient = 0.2274 at 25° C. for aqueous solutions of uni-univalent electrolytes.
 α^* = true degree of dissociation.
 β = second Onsager coefficient = 59.79 at 25° C. for aqueous solutions of uni-univalent electrolytes.
 γ = equivalent concentration.
 η = viscosity; molar fraction.
 ζ = Freundlich potential.
 κ = specific conductivity;
 constant of Debye-Hückel theory

$$= \sqrt{\frac{8\pi n_0 e^2 z^2}{DkT}} \text{ or } \sqrt{\frac{4\pi e^2}{DkT} \sum_i n_i z_i^2} \text{ or } \sqrt{\frac{4\pi e^2}{DkT}} 2\mu$$

 λ_c = ionic conductivity at a concentration c .
 λ_∞ = ionic conductivity at infinite dilution.
 μ = ionic product = $\frac{1}{2} \sum_i n_i z_i^2$.
 ν = frequency.
 ρ = electric density.
 σ = surface tension.
 τ = time of relaxation.

- ϕ = thermionic work function ;
 relative viscosity η_c/η_0 .
 ψ = potential at any point due to the solution.
 $\mathfrak{D}$ = differential diffusion coefficient.
 Λ = equivalent conductivity.
 Λ_∞ = equivalent conductivity at infinite dilution.
 $\log$ = logarithm to base 10.
 $\ln$ = natural logarithm.
 $pH = \log \frac{1}{\text{hydrion concentration}}.$
 $pK = \text{indicator exponent} = \log \frac{1}{\text{diss. const. of indicator}}.$
 $pT = \text{titration exponent} = pH \text{ at which an indicator is half dissociated.}$
 $rH = \log \frac{1}{\text{hydrogen pressure}}.$
 $pI = pH \text{ corresponding to the isoelectric point.}$
 $\nabla^2 = \text{Laplace's operator} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$
 $() = \text{activity of a species.}$
 $[] = \text{concentration of a species.}$
 $\Sigma = \text{summation of all types similar to type } i \text{ from } 1 \text{ to } s.$

CHAPTER I

HISTORICAL INTRODUCTION TO ELECTROCHEMISTRY

Early Electrochemical Experiments.

THE study of the phenomena exhibited by chemical substances when they are subjected to the action of electrical forces has been a comparatively recent development in the history of chemistry. The first important electrochemical investigations were made in 1776 by Cavendish, who measured the conductivities of aqueous solutions of chemical compounds.¹ In his apparatus the liquid resistance was contained in a long tube with movable wire electrodes thrust in at each end. One set of electrodes from two such tubes, the resistances of which were to be compared, were connected with the outside of a Nairne battery of Leyden jars, whilst the other electrodes were connected each to a separately insulated piece of tinfoil. Cavendish charged all the jars of the battery together to a known degree of electrification and shorted first one of the pieces of tinfoil through his body, then the other. By adjusting the lengths of the liquid columns he was able to judge when he received a shock of the same intensity from each, and so to compare the resistances of the two electrolytes. In spite of the very simple apparatus which he used, it is a tribute to the accuracy and care of his experiments that all his results were within 15% of the now accepted values. Cavendish's work, however, was not at the time extended to measurements on other substances, and investigations of electrochemical phenomena were not continued until, in 1800, the discovery of Volta's pile made it possible to obtain a steady current at will.

¹ "Scientific Papers of the Hon. Henry Cavendish" (Cambridge, 1921), Vol. 1, pp. 24, 25 and 311-334.

Galvani had observed that the leg-muscles of a recently dissected frog underwent contraction when connected, by metallic conductors, to specific nerves in the limb. He supposed this effect to originate from the energy stored by the muscular tissues, which was released during the experiment. Volta corrected this view and showed that the observed effect was due to electric currents, which flowed when the circuit was completed. Moreover, he could obtain exactly similar currents by the contact of two dissimilar metals separated by "moist conductors," such as filter-paper soaked in dilute acid. By constructing a pile of these units and connecting the ends through an external circuit, an electric current could then be obtained; the magnitude of the potential drop between the ends was determined by the number of units in the pile.

Almost immediately after its discovery, Nicholson and Carlisle in 1801 applied this new and powerful method to decompose water. Later, Davy used it for the electrolysis of aqueous solutions and fused moist alkalis.¹ But although Davy's experiments were much more exhaustive than those of earlier workers, he still had no means of measuring accurately the magnitude of an electric current. He was unable therefore from his observations to deduce any consistent relation between the amount of current passing and the extent of the chemical action produced.

Faraday's Laws of Electrodeposition.

The discovery of the principle of the galvanometer by Oersted gave Faraday the means for extending Davy's work and discovering the quantitative relationships for which Davy had sought. His results are well known, and are expressed in the two laws of electrodeposition which he formulated :

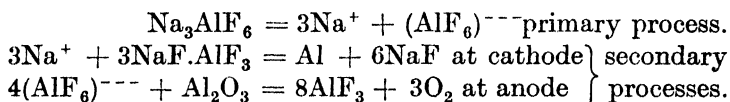
- (1) The amount of chemical deposition accompanying the passage of an electric current through a solution is proportional to the quantity of electricity which has passed.

¹ H. Davy, *Phil. Trans.*, **98** (1808), 1; Ostwald's "Klassiker der Exakten Wissenschaften," No. 45.

(2) If the same current be passed for the same time through a series of conducting solutions, the quantities of products liberated are proportional to their chemical equivalents.¹

These two laws may be summarised by stating that the passage of 96,450 coulombs of electricity² through a conducting solution always results in the decomposition of 1 gram-equivalent of the electrolyte. This quantity of electricity is known as the faraday.

Faraday emphasised the importance of realising that in all electrochemical processes, liberation of the products could take place only at the electrodes, and that the quantity of material deposited was entirely independent of all factors except the quantity of electricity passing. It is of course necessary to remember that the above laws apply only to the primary processes of electrochemical change, and the observed chemical effects may be complicated by a series of secondary processes resulting in quite different products. In the manufacture of aluminium, for example, purified bauxite is electrolysed after mixing it with cryolite as a flux. The following primary and secondary processes are supposed to take place :



Faraday avoided such secondary processes occurring in his experiments by electrolysing molten salts. He connected

¹ M. Faraday, "Experimental Researches in Electricity," Series v, June 1883. After stating that the sum of chemical deposition due to an unvarying current is constant for any section taken across a uniform conductor, Faraday writes :

"I have reason to believe that the statement might be still more general and expressed thus, 'That for a constant quantity of electricity whatever the decomposing conductor may be . . . the amount of electrochemical action is also a constant quantity —i.e., would always be equivalent to a standard chemical effect founded upon ordinary chemical affinity.'"

Later, in January 1834, Faraday succeeded in demonstrating this "law of definite action" from experiments on electrodeposition in fused salts.

² 96,450 coulombs is the present accepted value for this constant.

these in series with a water voltameter, which measured the quantity of electricity which passed. The deposition so obtained from fused tin salts gave a value for the electrochemical equivalent of tin agreeing with the chemical equivalent.¹

The full significance of Faraday's laws, however, was not pointed out until 1881, when Helmholtz,² in his Faraday Lecture, directed attention to the close resemblance between these laws of electrodeposition and Dalton's laws of constant and of multiple proportions. The first of Dalton's laws states that the proportion by weight of the elements in a given compound is in a fixed ratio. Faraday's first law asserts that the same amount of current is always required to deposit 1 gram-equivalent of an element. Moreover, according to the law of multiple proportions, when two elements combined forming more than one compound, if the weight of one was kept constant, the combining weights of the other were in simple numerical ratio with one another. Similarly, Faraday's second law implies that if the element deposited has more than one valency, the amounts of electricity required to cause the deposition of 1 gram-atom in each case are in simple ratio to one another. Dalton's atomic theory gives us an adequate explanation of the facts of chemical combination, and Helmholtz was led to the conclusion that there must be an atom or unit of electricity. An atom in the ionic state would then carry one or more of these fundamental units of electricity. If an atom has a valency n , each gram-ion has associated with it $n \times 96,450$ units of charge, and therefore dividing by Avogadro's number N , each single ion will carry a charge $\frac{n \times 96,450}{N}$ coulomb. Helmholtz's arguments thus constituted the first indication that an electron would be discovered to represent this unit of charge when dissociated from its ion. The actual discovery of the electron by J. J. Thomson was not made, however, until the end of the following decade.

¹ Faraday, "Experimental Researches," Notes 557-586.

² Helmholtz, *J.C.S.*, 39 (1881), 277.

The Theories of Grotthus and Clausius.

In 1805 Baron C. J. von Grotthus had put forward a theory of electrolysis which attempted to explain why the products of electrolysis should appear only at the electrodes. After Faraday's laws were established, his theory was found also to be capable of accounting for these, provided each ion of a molecule was supposed to possess a fixed charge. The stages which Grotthus supposed to take place during the electrolysis of a substance, were as follows :

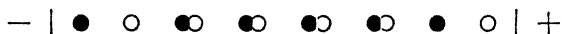
- (1) initially the molecules, consisting of both positive and negative ions, which will be represented respectively by ● and ○, existed unoriented in the medium



- (2) on applying the potential gradient throughout the liquid by connecting the electrodes to the opposite poles of a source of electricity, orientation of these molecules took place so that the negative ends were all directed towards the electrode where the current entered the solution and vice versa



- (3) This was followed by a decomposition of the end molecules next to the electrodes,



- (4) resulting in a change of partners, the positive and negative portions of the molecules which have been decomposed appropriating, respectively, the negative and positive portions of their adjacent undecomposed molecules. This process was then repeated along the line of molecules between the electrodes.



- (5) Re-orientation then took place to give the state equivalent to (2)



- (6) and the processes could be repeated to cause the decomposition of another molecule.

The theory is, however, open to a formidable objection. No current ought to flow until the electromotive force has exceeded such a value as is high enough to decompose the molecules at each end. In certain cases—as, for example, in the electrolysis of acidulated water using platinum electrodes—such definite decomposition voltages do appear, but these have been traced to the polarisation of the electrodes by accumulated films of electromotively active material, resulting from the decomposition. If these side effects are avoided with a “non-polarisable” cell such as



so that there is no chance of anything being deposited on the electrodes which is not already present in the solution, then the current flowing is strictly proportional to the E.M.F. in accordance with Ohm's law.

The weakness of Grotthus' theory is therefore that it supposes decomposition of the molecules of the electrolyte into charged particles to take place *after* the E.M.F. is applied. Clausius in 1857 realised that if Ohm's law could be exactly obeyed by a solution, charged particles, some positive and some negative, must already be present in the solution, although perhaps in quantities too small to be detected chemically. He supposed the free life period of these ions to be very small, their existence depending on the kinetic interactions between the molecules. Clausius was not able to prove that the quantities of ions present in the solution would be sufficient for the transportation of the electricity. If, however, such dissociation does take place, an electric field should cause a slight change in concentration of the electrolyte in the region of the electrodes, due to the motion of the ions towards the opposite poles. Faraday succeeded in detecting these changes in concentration and Hittorf, who measured them with a higher degree of skill, explained them by assuming that the positive and negative ions moved through the solution with unequal velocities. It appears therefore that electrolytic dissociation in solution is at least highly probable, although the Clausius theory of its mechanism is not satisfactory.

The Electrical Conductivities of Solutions.

At this point we may consider some important experimental work which was carried out by Kohlrausch between 1869 and 1880. He made an extensive study of the variation of the conductivity of electrically conducting solutions with concentration and temperature.¹ In order to express electrical conductivity, he considered the reciprocal of the specific resistance (*i.e.*, the resistance of the solution between opposite faces of a cube having edges 1 centimetre long and with a potential difference of 1 volt across the faces). This "specific conductivity" has therefore the dimensions of a current. Now Kohlrausch discovered that the specific conductivity κ changed with concentration, and it was useless in defining the variation in the conductivity of the gram-molecule of electrolyte. For this purpose the conductivity is better expressed in terms of the "equivalent conductivity"—*i.e.*, as the current flowing between two electrodes 1 cm. apart with a potential difference of 1 volt between them, the area of the electrodes being adjusted so that the solution between them contains 1 gram-equivalent of the substance. If, then, the concentration of the solution is c gram-equivalents per 1,000 c.c. the concentration is equal to $c/1,000$ gram-equivalents per cubic centimetre and $1,000/c$ c.c.s will contain 1 gram-equivalent. The area of the electrodes to contain between them 1 gram-equivalent of substance when they are 1 cm. apart would therefore have to be $1,000/c$ sq.cm.—*i.e.*, the equivalent conductivity Λ of the solution will be $1,000\kappa/c$.

Kohlrausch measured this quantity, and found that it increased with increasing dilution and tended to a constant limiting value at high dilutions. The specific conductivity, however, in general falls with increasing dilution, although in the case of very soluble salts the variations of κ with concentration may be more complicated (Fig. 1). The relation between the equivalent conductivity and dilution was found to vary with the nature of the electrolyte. For strong electrolytes, Kohlrausch proposed two empirical

¹ Kohlrausch and Holborn, "Leitvermögen der Elektrolyte, insbesondere der Lösungen," Leipzig, 1916.

laws,¹ according to which the equivalent conductivity of the solution was proportional either to the square root or to the cube root of the concentration. The latter rule was recommended as being the more applicable in concentrated solutions.² The square-root law

$$\Lambda = \Lambda_{\infty} - kc^{\frac{1}{2}} \quad . \quad . \quad . \quad (1)$$

has since been shown to have a theoretical basis for very dilute solutions (see Chapter VII). From equation (1) the value of the equivalent conductivity at infinite dilution Λ_{∞} , for aqueous solutions of strong electrolytes may be obtained by extrapolation of the experimental results to

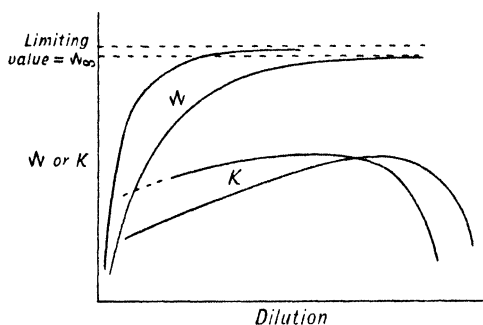


FIG. 1.—THE EFFECT OF DILUTION ON EQUIVALENT AND SPECIFIC CONDUCTIVITIES.

zero concentration. It will be seen presently that this constant is a very important one in the theory of electrolytes.

This is true only for strong electrolytes. For weak electrolytes, such as the organic acids, the equivalent conductivity shows no tendency to reach a limiting value as the concentration decreases, and it is not therefore possible to obtain a value for the equivalent conductivity at infinite dilution from these measurements (Fig. 2). Kohlrausch found, however, that for all solutions of electrolytes for which he could determine the equivalent

¹ Kohlrausch, *Wiss. Abh. Tech. Reichsanst.*, **3** (1900), 156.

² Kohlrausch and Holborn, *loc. cit.*, p. 107. Kohlrausch proposed the cube-root law after observing that the plot of equivalent conductivity against the square root of the concentration, although linear in many cases over a considerable concentration range, fell away from linearity in strong solutions.

conductivity at infinite dilution, this quantity could be represented as the sum of two parts. One of these parts he attributed solely to the effect of the cation, and the other to the effect of the anion. Thus for the equivalent conductivities at infinite dilution of the salts

$$\begin{array}{rcl} \text{KCl} = 149.82 & \text{NaCl} = 126.42 & \text{Difference } 23.40 \\ \text{KNO}_3 = 144.92 & \text{NaNO}_3 = 121.51 & \text{Difference } 23.41 \end{array}$$

the difference must in each case be that between the conductivities at infinite dilution of the sodium and

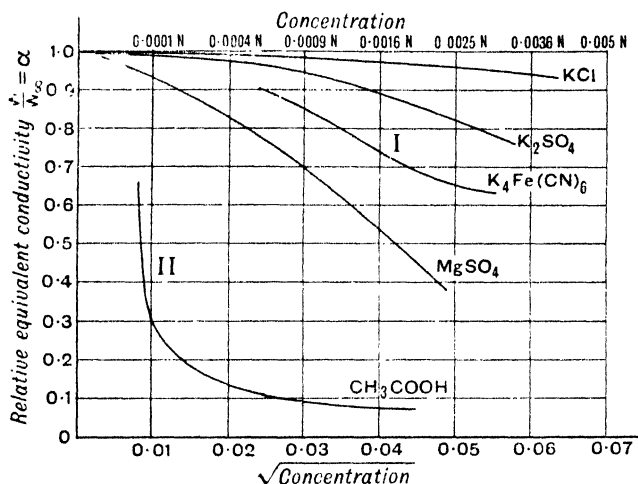


FIG. 2.—EQUIVALENT CONDUCTIVITIES IN DILUTE SOLUTIONS.

potassium ions. The conductivity property of ions seems therefore to be additive at infinite dilution. Kohlrausch summarised this in the law of independent ionic mobilities,¹

$$\Lambda_{\infty} = (\lambda_{-})_{\infty} + (\lambda_{+})_{\infty} \quad . \quad . \quad . \quad (2)$$

Here $(\lambda_{-})_{\infty}$ and $(\lambda_{+})_{\infty}$ represent the contributions to the limiting value of the equivalent conductivity due respectively to the anion and cation of the electrolyte. Raoult showed later that this additive property of the ions at infinite dilution could be extended to most of the physical properties of

¹ Kohlrausch, *Wied. Annalen*, 6 (1879), 145; 26 (1885), 161, 123.

electrolytes,¹ and it must therefore be given careful consideration in formulating any theory of electrolytes.

While Kohlrausch was carrying out his work on the conductivities of electrolytes, some interesting conclusions were reached from a study of their chemical properties. In an attempt to determine the "avidities" of acids relative to one another, Thomsen² had found that in the neutralisation of 1 gram-molecule of a "strong" acid (*i.e.*, one whose conductivity curve came in the first class illustrated above) with 1 gram-molecule of a "strong" base the heat of neutralisation was practically constant. Moreover, the lower the heat of neutralisation of an acid for the same base, the lower was its avidity, or strength. Arrhenius,³ too, had observed from his work on the equivalent conductivities and chemical avidities of several acids that, in solutions of the same concentration, these two properties showed parallel variations from one acid to another. He communicated his results to Ostwald, whose subsequent work showed that the catalytic activity of acids on certain reactions such as the inversion of cane-sugar or the hydrolysis of esters corresponded with the order of their conductivities.

van 't Hoff's Law.

Pfeffer in 1887 demonstrated that electrolytes in solution gave abnormally high values for their osmotic pressures. Now, van 't Hoff had formulated the law that, in dilute solutions of non-electrolytes like sugar, the osmotic pressure obeyed a similar law to that of the gas pressure at low pressures. He therefore included the exceptions for electrolytes in the general formula :

$$PV = iRT \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where i represented the degree of abnormality shown by the osmotic pressures of these substances. In this equation i was equal to unity for solutions of non-electrolytes.

¹ Cf. also additivity of the refractivity of ions at infinite dilution : K. Fajans, *Trans. Faraday Soc.*, **23** (1927), 363.

² J. Thomsen, "Thermochemische Untersuchungen," 1882-1886.

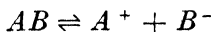
³ Arrhenius, *Z. physikal. Chem.*, **1** (1887), 631; "Text-book of Electrochemistry," trans. John McCrea (London, 1902), Chapter X.

The Arrhenius Dissociation Theory of Electrolytes.

In order to explain these facts relating to the physical and chemical properties of solutions of electrolytes, Arrhenius in 1886 put forward his theory of electrolytic dissociation. He supposed that the electrolyte could exist in two forms independent of one another and without the application of any electric forces to the solution. One of these forms he associated with the molecule, the other with the ions. The two species, molecules and ions, were then assumed to exist together in the solution in equilibrium with one another. The ratio of the electrolyte in the dissociated or ionic form to that in the molecular uncharged form was called the degree of dissociation α . Now, since only that part of the electrolyte present in the solution as charged ions could be responsible for the passage of the current, the equivalent conductivity at any dilution must, according to Arrhenius, be proportional to the degree of dissociation α at that dilution. The constant of proportionality may be determined from the limiting conditions—namely, that the maximum conductivity Λ_{∞} which is observed at infinite dilution must correspond to the existence of the electrolyte solely in the charged ionic form, *i.e.*, to the complete dissociation of the molecular form of the electrolyte. Thus when $\alpha = 1$ $\Lambda = \Lambda_{\infty}$, and in general, therefore

$$\alpha = \frac{\Lambda}{\Lambda_{\infty}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If electrolytes exist in two forms which are in equilibrium with one another, it should be possible to apply the law of mass action to the dissociation equilibrium. For the dissociation of 1 gram-molecule of an electrolyte AB into cations A^+ and anions B^- in a solution of dilution V , we have :



At equilibrium, the fraction of a gram-molecule of the undissociated form present will be $1 - \alpha$ and its concentration therefore $\frac{1 - \alpha}{V}$. So for the ionic species present, their concentrations at equilibrium will be $\frac{\alpha}{V}$: applying the

principle of mass action and calling the mass constant for the ionic equilibrium the "dissociation constant", K_{diss} , we obtain Ostwald's dilution law :

$$\left. \begin{aligned} K_{\text{diss}} &= \frac{[A^+][B^-]}{[AB]} \\ \text{or } K_{\text{diss}} &= \frac{\left(\frac{\alpha}{V}\right)\left(\frac{\alpha}{V}\right)}{\left(\frac{1-\alpha}{V}\right)} = \frac{\alpha^2}{V(1-\alpha)} \end{aligned} \right\} \quad \cdot \quad \cdot \quad (5)$$

or, substituting in this equation the value of α from the Arrhenius equation (4) :

$$K_{\text{diss}} = \frac{\Lambda^2}{\Lambda_{\infty} V (\Lambda_{\infty} - \Lambda)} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

For weak electrolytes the degree of dissociation is, according to Arrhenius, small and it is therefore possible as a first approximation to put unity in place of $1 - \alpha$. Thus, for this class of electrolytes, we may write :

$$\alpha = \frac{K}{\sqrt{\text{concentration}}} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

Ostwald's measurements of the conductivities of weak organic acids¹ show that the dissociation constant in the dilution equation is very nearly constant over a large range of concentrations. For electrolytes like dichloroacetic acid, however, which are only slightly stronger than the simple organic acids, the deviations from the dilution law become more marked (Table I). Thus even with some "weak" electrolytes the dilution law is adhered to only very approximately. Many empirical equations have been suggested to represent the results for these electrolytes which do not obey Ostwald's law. van 't Hoff² and Rudolphi³ proposed an equation of the form :

$$K_{\text{diss}} = \frac{\alpha^2}{(1-\alpha)V^{\frac{1}{2}}} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (8)$$

¹ W. Ostwald, *Z. physikal. Chem.*, **3** (1889), 170, 241, 369.

² van 't Hoff, *ibid.*, **18** (1895), 300.

³ Rudolphi, *ibid.*, **17** (1895), 385.

which accounted with fair accuracy for the behaviour of many weak electrolytes which did not accurately follow Ostwald's dilution formula. Van Laar¹ pointed out, how-

TABLE I
Ostwald's Dilution Law

Sub-stance.	Acetic acid $\Lambda_{\infty} = 364$.			Dichloroacetic acid $\Lambda_{\infty} = 361$.		
Dilu-tion V .	Equiva-lent conduc-tivity.	$\frac{\Lambda}{\Lambda_{\infty}} = \alpha$.	$K = \frac{\alpha^2}{(1 - \alpha)V}$	Equiva-lent conduc-tivity.	$\frac{\Lambda}{\Lambda_{\infty}} = \alpha$.	K_{Ostwald} .
8	4.34	0.0119	0.0 ₄ 179	—	—	—
16	6.10	0.0167	0.0 ₄ 177	—	—	—
32	8.63	0.0237	0.0 ₄ 180	25.31	0.0702	0.0 ₃ 166
64	12.09	0.0332	0.0 ₄ 178	29.07	0.0805	0.0 ₃ 110
128	16.99	0.0477	0.0 ₄ 186	31.75	0.0838	0.0 ₄ 597
256	23.82	0.0655	0.0 ₄ 175	33.70	0.0987	0.0 ₄ 378
512	32.20	0.0878	0.0 ₄ 165	35.2	0.0995	0.0 ₄ 206
1024	46.00	0.1260	0.0 ₄ 165	36.01	0.0999	0.0 ₄ 105

ever, that considerable errors could be introduced in the calculation of the degree of dissociation from equation (4)

$$\alpha = \frac{\Lambda}{\Lambda_{\infty}}$$

since the values of Λ_{∞} for weak electrolytes were not then known with any great degree of accuracy. The errors in α would be considerable particularly when α had higher values than those for the simple organic acids. The agreement obtained at different concentrations in certain cases between the values of K_{diss} calculated from the van 't Hoff-Rudolphi formula may therefore be a consequence of the method used in calculating α for these electrolytes.

Now, we have already seen that electrolytes do not obey the normal osmotic pressure law which is exactly similar to the perfect gas law $PV = RT$, but that the deviations can be summarised in the equation

$$PV = iRT \quad . \quad . \quad . \quad . \quad . \quad (9)$$

¹ van Laar, *Archives Musée Teyler*, Series ii, 7 (1902), 59.

where i , the "degree of abnormality," is a quantity varying with the concentration and with the electrolyte. Osmotic pressure is due to the kinetic bombardment of the dissolved particles in a solution, and if dissociation of an electrolyte takes place in solution, the increased number of particles will result in a higher osmotic pressure. Obviously there should be some direct relation between the factor i and the degree of dissociation of an electrolyte which determines the number of particles present. To find this let us suppose an electrolyte, upon complete dissociation, gives rise to n ions (e.g., with CaCl_2 , n would be equal to three); then, when the degree of dissociation is α , the number of non-ionised particles present per initial gram-molecule will be $N(1 - \alpha)$ and the number of ionised particles will be $Nn\alpha$, where N is Avogadro's number. The total number of particles of all species now present in the solution is $nN\alpha + N(1 - \alpha)$, in place of the N particles which would have been present had no dissociation taken place. The ratio of these numbers will be the factor by which the osmotic pressure of the electrolyte is abnormal and fails to conform to Raoult's law—i.e.:

$$i = n\alpha + (1 - \alpha) \quad . \quad . \quad . \quad (10)$$

$$\text{or } \alpha = \frac{i - 1}{n - 1} \quad . \quad . \quad . \quad (11)$$

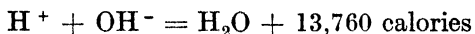
This equation was first obtained by Arrhenius. It gives a quantitative relation between the degree of dissociation of an electrolyte and the degree of abnormality in any of its osmotic properties. The values of i could be calculated by the above equation, from conductivity measurements which give α , or they could be determined directly from the freezing-point data. Good agreement was obtained by the two methods for many of the electrolytes studied, and this seemed to support the ideas of Arrhenius' dissociation theory that electrolytes can exist in solution either in the ionised or in the molecular form.

Failure of the Arrhenius Theory.

The Arrhenius theory was extremely valuable for many years after it had been put forward, in helping to clarify

experimental work. But it is open to criticism on many points where it will not account completely for the experimental evidence. At the time when it was put forward, many arguments were brought against it by contemporaries of Arrhenius, but nearly all of these have since proved quite unjustified, and the theory survived them to be of great value during the latter part of the nineteenth and the beginning of the twentieth centuries. There is, however, one feature in which the theory has always been a complete failure. This is its inability to account for the anomalous behaviour of strong or even of moderately strong electrolytes towards the dilution law, for it does not suggest that the behaviour of solutions of strong electrolytes should differ from that of weak electrolytes like acetic acid. The values of α , the degree of dissociation, calculated from measurements of osmotic phenomena (giving i) and from conductivity measurements, show quite good agreement for weak electrolytes. The results which have been quoted show that it is only for a limited class of very weak electrolytes that K_{diss} , calculated from these values of α , is constant over a wide range of concentration, whilst for stronger acids K_{diss} is no longer constant.

There are other difficulties which have only become fully apparent more recently. Thus, the heats of neutralisation of strong acids with a strong base should, according to the dissociation theory, show some variation from acid to acid since the heat evolved from the reaction



during the neutralisation will depend on the quantity of hydrogen ion present, and hence on the degree of dissociation of the acid. It was, for example, well known that the halogen acids did not possess the same degrees of dissociation in solutions of the same normality, yet the measurements of the heats of neutralisation of these at 20° C. with various "strong bases," made by an adiabatic calorimetric method, gave singularly consistent results¹ (see Table II).

¹ T. W. Richards and Rowe, *J. Amer. Chem. Soc.*, **42** (1920), 1621; *ibid.*, **44** (1922), 684.

TABLE II

Heats of Neutralisation of Strong Acids and Bases

Acids and bases.	Degree of dissociation of acid in $M/100$ solutions. ¹	Degree of dissociation of base in $M/100$ solutions. ¹	Heat of neutralisation in $M/100$ solutions.
HCl and KOH .	0.963	0.955	14,007
HCl and NaOH .	0.963	0.953	13,888
HCl and LiOH .	0.963	0.955	13,985
HBr and KOH .	0.964	0.955	13,981
HI and LiOH .	0.963	0.955	13,918
HNO ₃ and NaOH .	0.983	0.953	13,830

These measurements were claimed to have an experimental error not exceeding about 0.05%, yet in the last case of the neutralisation of nitric acid with caustic soda, where there are, according to Arrhenius, more hydrogen ions present, the heat of neutralisation is actually smaller than in the case of those acids with a lower degree of dissociation.

There is another important set of facts which can receive no explanation in terms of the simple dissociation theory. The fraction of the current carried by a particular ion in a solution is called the transport number. If dissociation takes place with increasing dilution, this will influence the number of ions present, but it will have no effect on the ratio of the number of a particular ionic species to the total number of ions present, and it should not therefore have any influence on the transport numbers. Experimental evidence for a variation in transport numbers with concentration was, however, found by Steele in 1901,² and more accurate measurements of the transport numbers have shown that this variation with concentration follows a very complicated function which could not possibly be accounted for in terms of the simple dissociation theory.

It may appear from the criticisms of the Arrhenius theory which must be made in the light of more recent knowledge, that there is little experimental evidence left to justify

¹ These values for the degrees of dissociation are calculated by means of the conductivity formula from the limiting conductivities at infinite dilution.

² Steele, *Phil. Trans. (A)*, **198** (1902), 105.

such a view of ionic dissociation. But, although it has been superseded by a new and more effective dissociation theory, the simple ionic theory succeeded in correlating what had previously been quite isolated phenomena. The new theory which we shall now refer to, could never have been formulated except on the foundations of Arrhenius' work, and its value rests upon the fact that it is an extension and revision of the former view.

The Theory of Complete Ionisation.

It is evident from the experimental results just given that some extension had to be made in the ideas of electrolytic dissociation, but it is important to realise not only how but just where this extension had to be made. Arrhenius distinguished two quite separate phases in ionic dissociation : firstly, the existence of ions in a solution quite irrespective of any electrical forces and secondly, the existence of two molecular species in an electrolyte solution independent of one another. The first of these species he supposed to behave as ideal solute molecules, whilst the other species dissociated into ions which behaved singly as ideal solute molecules. It was this second part of the theory which, being capable of quantitative interpretation, was followed up and became known as the Arrhenius dissociation theory, but the first clause is as valid in the light of recent experimental work as when it was stated. The second clause, however, has been rejected in favour of a theory of complete dissociation in solution. The properties of electrolytes can therefore no longer be explained in terms of an increase in dissociation with increasing dilution, and some quite different mechanism must operate. van Laar¹ first made it clear that, on account of the strong electrostatic forces which exist between ions in solutions of strong electrolytes, these ions cannot exist independently and behave as ideal solute molecules in the manner assumed by Arrhenius. A few years later it was claimed that electrostatic attraction was sufficient to account for all the behaviour of strong electrolytes,²

¹ van Laar, *Archives Musée Teyler*, Series ii, 7 (1902), 59.

² Bjerrum, *Proc. 7th Int. Congress Chemistry*, x (1909).

and in 1912, Milner carried out an analysis of the distribution of ions in solutions of strong electrolytes assuming complete ionisation, from which the osmotic properties of these solutions could be calculated.¹

The evidence for this complete ionisation of electrolytes in solution has now become so great that there can be no doubt that the simple Arrhenius dissociation theory was based upon a misconception of the true state of affairs in solutions of strong electrolytes. Noyes² in 1904 called attention to some experimental evidence for the absence of unionised molecules of electrolytes in solutions. The optical activity and the colour of salts, when these properties were referred to equivalent quantities, were found to be independent of the Arrhenius degree of dissociation, and to be additive with respect to the properties of the constituent ions even up to quite high concentrations. This view has been confirmed by the classical work of Bragg on the analysis of crystal structure³ which has shown that, in crystals of polar substances like sodium chloride, the ions of sodium and of chlorine are the only species which build up the lattice, and that these ions are kept in their mean positions by the electrostatic forces and repulsive forces between them. In the particular case of sodium chloride and similar crystals which have a face-centred lattice, the two ions occur alternately and there is therefore no particular sodium ion more completely associated with one chlorine nearest neighbour than with any of the other five. There is, in fact, no molecule of sodium chloride as such in the lattice. When the substance is dissolved in a polar solvent, the ions will be given an independence of motion, for the electrostatic forces between them will be decreased due to the large increase in the dielectric constant of the intervening medium. Only in very strong solutions, where the ions of sodium and chlorine come sufficiently close to one another for electrostatic forces between them to be appreciable, will these

¹ S. R. Milner, *Phil. Mag.*, **23** (vi) (1912), 551.

² A. A. Noyes, *Science*, **20** (1904), 584.

³ Sir W. H. Bragg and W. L. Bragg, "The Crystalline State," Vol. I (1934); Sir W. H. Bragg, "Introduction to Crystal Structure" (1928).

oppositely charged particles begin to move about together as an "ion-pair." Even where this pairing or grouping of ions takes place in strong solutions, the component ions of a group will continually change places with other ions from the surrounding medium. The solution will therefore have a degree of dissociation only in the sense that there is a greater or smaller proportion of these ion groups present in the solution. These cannot of course contribute to the conductivity because they are, on the whole, neutral.

Hill¹ has suggested the use of the partition coefficient as a method for examining the properties of an electrolyte, provided the solvent used will dissolve the electrolyte in its non-conducting form. Silver perchlorate is particularly suited to distribution experiments, since it is a strong electrolyte in aqueous solution and will dissolve in a non-conducting form in benzene or chloroform. A determination of the molecular weight by freezing-point measurements in benzene has shown that the salt always has a molecular weight in this solvent corresponding to an average molecular complexity greater than unity and rising to a maximum of 2.2 with increasing concentration. This increasing molecular complexity must be attributed to the formation of associated molecules and its occurrence in this particular case rather complicates the main argument. However, if benzene is shaken with an aqueous solution of silver perchlorate, a unimolecular silver perchlorate phase distributes itself such that the ratio of the concentration of perchlorate in benzene (allowing for association) to its concentration in water, is a constant. When this partition coefficient is used, it is found that the concentration of perchlorate molecules in the water must be considerably less than 1% of that calculated from conductivity data. The measured conductivity must therefore be due entirely to the ions formed from the completely dissociated silver perchlorate.

Still more direct evidence for the state of electrolyte molecules in solution is available from a study of the Raman spectra of the solutions.² Although measurements may be

¹ A. Hill, *J. Amer. Chem. Soc.*, **43** (1921), 204.

² L. A. Woodward, *Physikal. Z.*, **32** (1931), 777.

made only in fairly concentrated solutions, no lines other than those for the solvent and the ions of the electrolyte have been observed for solutions of NaOH, KCl, HCl, HI, or KCN. If these substances existed in the solutions in an undissociated state, a line characteristic of the new vibration would appear. In the case, however, of sulphuric and nitric acids, and particularly of mercuric salts, which, from conductivity measurements, appear to behave as weak electrolytes, new lines were observed in the Raman spectra which had to be associated with the existence of undissociated molecules in the solution.¹ Raman lines observed in the spectra of the chlorides of non-metals, which must be due to a direct link between the chlorine and the element, do not appear at all in the spectra of many of the metal chlorides. Moreover, the evidence of optical measurements of the refractivities² and of the absorption spectra of some common strong electrolytes shows that the concentrations of undissociated molecules present must certainly be very small. Together with the analysis of crystal structures by the use of X-rays, these results clearly suggest a fundamental difference in structure between strong and weak electrolytes. Only the former are completely ionised in solution, and it is only for this class that a completely new dissociation theory is required. But although the Arrhenius dissociation theory is still preserved for weak electrolytes, the application of the simple mass law, even to these cases, has to be modified by introducing "activity coefficients" which are themselves functions of the concentrations of the ions present.³ These adjustable constants allow the simple formulae, derived by assuming ideal conditions to be used when the solutions no longer obey the ideal laws.

The Ion Atmosphere Theory.

Now, if complete ionisation takes place in solution, the electrostatic forces will result in a particular distribution of the ions throughout the solution. Debye and Hückel in

¹ See also von Halban, *Z. Electrochem.*, **34** (1928), 489.

² K. Fajans, *Trans. Faraday Soc.*, **23** (1927), 357.

³ D. A. MacInnes, *J. Amer. Chem. Soc.*, **43** (1921), 2048.

1923 gave an analysis of the specific distribution principle which enabled them to calculate the free energy of the solution and its conductivity¹ (see Chapters III and VII), but the qualitative consequence of complete ionisation may readily be predicted. The fundamental conception of the theory is that the attractive and repulsive forces on an ion due to the charges in its neighbourhood do not cancel out. In an electrically neutral solution containing positive and negative ions, each ion will attract to itself only those of the opposite sign. Around every positive ion in the solution there will therefore be an unsymmetrical charge distribution

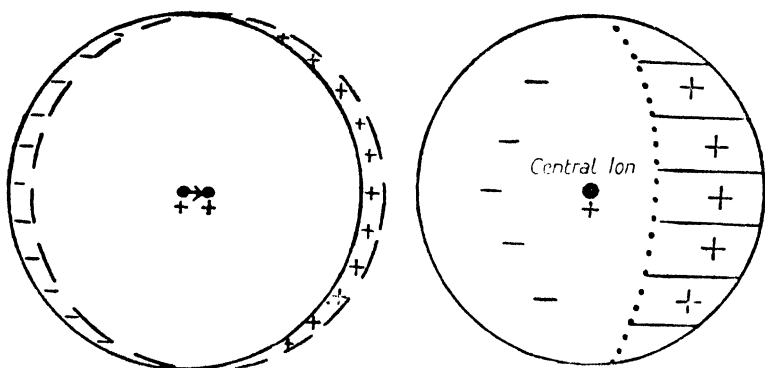


FIG. 3.—ION ATMOSPHERE ROUND AN ION.

or an “ion atmosphere” which is predominantly negative (round a negative ion this charge distribution will, predominantly, be positive). Now let us consider what will happen when an electric field is applied to the solution. While an ion will be attracted to one electrode, its atmosphere will tend to move in the opposite direction because of its opposite charge. The atmosphere which is now displaced from its neutral position will attract the central ion (see Fig. 3), so that the latter will suffer a retarding force during its passage through the solution. This relative displacement of an ion and its atmosphere under an external force is known as the “disymmetry effect.” Furthermore, ions in solution are associated with a certain quantity of solvent. The

¹ P. Debye and E. Hückel, *Physikal. Z.*, **24** (1923), 185, 305; P. Debye, *ibid.*, **25** (1924), 97.

excess of ions of opposite sign in the atmosphere will therefore cause the solvated ion to be moving in a region where the solvent is drifting relatively in the opposite direction. The "electrophoretic effect" which is so set up supplements the retarding action on the ion due to the disymmetry effect. Also since the thickness of the ion atmosphere is determined partly by the concentration and the valency of the ions, the mobilities of the ions must depend on these factors.

The method used by Debye and Hückel in applying these principles allowed the calculation of the properties of electrolytes to be made only at very low concentrations. New experimental methods for measuring the properties of very dilute solutions have, however, given results in general conformity with the theory, and the principles of the new dissociation theory have therefore been vindicated for the limiting case of these dilute solutions. In more concentrated solutions, where the ideal model postulated by Debye can no longer be supposed to hold, the possibility of the existence of both Coulomb and repelling forces of the van der Waals type must be taken into account.¹ As a consequence of the former, it would be expected that in solutions not at limiting dilutions, ion association between the ions of opposite charges would take place. This ionic association, which has been postulated by Bjerrum and Fuoss to account for the failure of the Debye-Hückel theory in strong solutions, is not necessarily confined in its complexity to the formation of ion pairs. At the same time it does not invalidate the theory of complete ionisation. The apparent paradox lies in the fact that the component ions of an ion group may constantly be changing places with other free ions from the solution, or even with those from other ion groups. The term "degree of dissociation" therefore assumes a new meaning. It no longer means, as Arrhenius made it mean, the fraction of charged particles in the solution. It must now be considered to measure the relative number of only those ions which, by remaining unassociated in pairs or groups, are able directly to contribute towards the con-

¹ O. Halpern, *J. Chem. Physics*, 2 (1934), 85.

ductivity. This new physical assumption then gives at once an explanation for the values of the equivalent conductivity which as the concentrations of the solutions increase fall more and more below the values calculated from Debye and Hückel's limiting law. For in these stronger solutions ion association will remove more and more ions from the number capable of contributing directly to the passage of the current.

The Thermodynamics of Electrolytes.

At the same time as these theories were put forward to explain the conductivity properties of electrolytes, the new science of thermodynamics was being developed, largely by the work of Gibbs, van 't Hoff, and Nernst. If the law of conservation of energy is applied to the chemical reaction occurring in a voltaic cell, it appears that the chemical energy used up in the battery should be equal to the electrical energy produced. This, however, fails to take into account either of the following two possibilities :

- (1) that the total energy available may appear partly as heat energy ;
- (2) that any heat energy stored in the cell may, during the reaction, appear as electrical energy.

The real solution of the problem was given independently by Gibbs¹ and Helmholtz.² It brought the operation of an electric battery into full accord with the laws of thermodynamics and with the theory of energy, although this use of thermodynamics, giving only a statistical view of the processes, leaves the question of mechanism unsolved.

In the galvanic cell—i.e., a cell in which a chemical reaction is caused to proceed with evolution of energy—the mechanism by which the E.M.F. is developed has been a much-debated problem. The application of thermodynamics shows that the electrochemical potential of a metal electrode in a cell is equal to the potential of its ions in the solution, and this fact enables the electrical energy

¹ J. Willard Gibbs, "Collected Works," Vol. I, pp. 331–349.

² Helmholtz, *Sitzungsber. der Berl. Akad.*, 1 (1882), 22.

to be expressed directly in terms of the energy changes taking place. At the same time, the values of the contact metal-metal potentials (the so-called volta potentials which always appear when the E.M.F. of a galvanic cell is measured) are very nearly equal to those observed for the potentials of the whole galvanic cell having these metals as electrodes.¹ The anomaly was resolved only when it was realised that the function of the metal-metal junction is to rearrange the electron energy levels in the two metals until the chemical reaction in the cell can take place.² The two aspects are not mutually exclusive, but both play a definite part in explaining the mechanism of the galvanic cell.

Accurate experimental work has shown, however, that a modification is necessary in the thermodynamic treatment in order to bring the theory into accord with the facts. Early thermodynamical methods assumed the validity of the simple gas laws which apply accurately only over a very limited range of the lowest concentrations. Deviations from these laws are apparent at all ordinary concentrations, but the exact nature of the deviations cannot be predicted by the kinetic theory. The continued use at ordinary concentrations of concentration terms in thermodynamic expressions based on the simple gas laws would therefore lead to errors, and Lewis³ proposed replacing the concentration terms by activities. The activity itself was defined as a function of the concentration such that by its direct substitution for the concentration, the simple expressions derived from the ideal laws held at all concentrations. Measurements of the electromotive forces in galvanic cells provide an accurate method by which the values of these activities may be estimated. Moreover, by means of the ion atmosphere theory, expressions have been obtained relating the activity to the concentration, which express experimental results accurately at concentrations where the theory may be applied.

The modern dissociation theory thus explains both the thermodynamic properties of ions and electrolytic irreversible

¹ E. K. Rideal, *Trans. Faraday Soc.*, **19** (1924), 617.

² Gurney, *Proc. Roy. Soc., A*, **136** (1932), 378.

³ G. N. Lewis, *Proc. Amer. Acad. Arts Sci.*, **43** (1907), 259.

processes such as the movement of ions under the influence of imposed electrical forces (conductivity) or shear forces (viscosity). For the purposes of theoretical considerations, therefore, there is no arbitrary difference between the study of the thermodynamic and the irreversible processes taking place in electrolytes. The data from both may now be interpreted in terms of the new dissociation theories.

CHAPTER II

FUNDAMENTAL ELECTRICAL MEASUREMENTS

Two important experimental methods have been used to study the electrochemistry of solutions. The first is the measurement of the conductivity and allied properties of a solution. The second is the measurement of the thermodynamic properties of a solution and in particular the electromotive forces developed between a standard electrode and an electrode in equilibrium with the solution. The conductivity and the viscosity of a solution are irreversible processes about which no theory can be formulated using thermodynamics. The processes involved in the measurements of the electromotive forces of reversible cells and the thermodynamic properties of a solution are, however, completely reversible, and the use of thermodynamics in solving these problems is perfectly justified. We shall first be concerned with the irreversible properties of electrolytes.

Coulometry.

The measurement of conductivity involves primarily the accurate measurement of a quantity of electricity, and this is always accomplished by using the principle of Faraday's first law. According to this law, the mass of the deposit from an electrolyte is directly proportional to the quantity of electricity passing. This quantity of electricity may be measured, therefore, in any apparatus in which the chemical deposit resulting from the passage of an electric current can be weighed. Such an instrument is called a "voltameter" or a "coulometer." The unit quantity of electricity, the faraday, is so universal a constant that the precise determination of its value becomes a matter of the greatest importance, and considerable attention has there-

fore been given to the design of accurate coulometers. It will be remembered that the faraday is defined as that quantity of electricity which will cause the deposition of 1 gram-equivalent of any substance or element.

The Silver Coulometer.

Silver was considered by Rayleigh to be the most convenient substance which could be weighed accurately, after electrochemical deposition.¹ In his coulometer he made use of the deposition of silver from silver nitrate solution for measuring the quantity of current. The anode was enclosed in a filter-paper bag, since if the same solution was used for electrolysis without this precaution, the deposits became steadily heavier for the passage of the same quantity of electricity.² The effect has been traced to the formation of acid at the anode, which may cause a heavier silver ion than Ag^+ (e.g., Ag_2^{++}) to be produced from a subsalt of silver. This error is eliminated by enclosing the anode in a vessel which allows conduction but prevents convection. Slight differences in osmotic pressure which arise from changes in concentration in the two vessels are then also in such a direction as to cause liquid to flow into the anode vessel. Unfortunately, filter paper has been shown to have a definite chemical activity, and its use could not therefore give the most accurate results.³ Fig. 4 shows the type of apparatus which Richards used to overcome the inaccuracies in Rayleigh's instrument.⁴ *E* is the cathode vessel, which, before

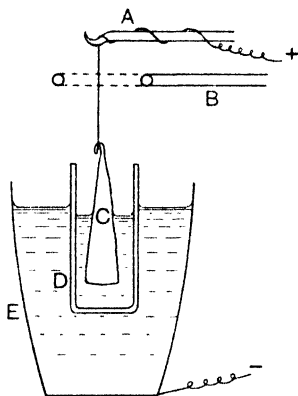


FIG. 4.—RICHARDS' SILVER COULOMETER.

¹ Lord Rayleigh and Mrs. Sidgwick, *Phil. Trans. (A)*, **175** (1884), 458.

² Rodger and Watson, *ibid.* (A), **186** (1898), 636.

³ E. B. Rosa and E. W. Vinal, *Bull. Bureau Standards*, **9** (1913), 151.

⁴ T. W. Richards, Collins and Heimrod, *Z. physikal. Chem.*, **32** (1900), 336; *Proc. Amer. Acad. Arts Sci.*, **35** (1899–1900), 123.

an experiment, was carefully cleaned and dried, and this contained the chemically pure silver nitrate solution. Since the silver was deposited on the cathode, it had to be weighed very accurately. The greatest precautions had therefore always to be observed to avoid any contamination of the cathode which might cause an alteration in its mass. The anode liquid was contained in the porous pot *D*, and its level was always kept below the level of the liquid in the cathode vessel, so that any diffusion of liquid took place inwards, and not outwards. The anode *C*, a lump of electrolytically pure silver, was hung from an insulated glass rod by a metal suspension connected to the positive end of the apparatus in which it was desired to measure the quantity of electricity flowing. Using absolutely pure silver nitrate and pure silver, the results with Richards' coulometer are reproducible to within 1 part in 10,000. The small error is due to the inclusion of water and silver nitrate in the silver deposited, the magnitude of the inclusion being proportional to the area of surface on which the silver is being deposited.

The Absolute and International Units of Electricity.

If the coulometer is used to determine the absolute quantity of electricity, a galvanometer must be introduced into the circuit to give the absolute value of the current. This instrument must therefore be calibrated on the absolute scale.¹ The principle adopted in carrying out this calibration depends on the use of the magnetic fields set up in a solenoid due to the passage of an electric current. Thus, when a current is passed in opposite directions through two double cylindrical coils one within the other, the inner of these, wound as a uniform solenoid on an ebonite ring (and therefore equivalent to a simple magnet), suffers a co-axial magnetic attraction. This attraction may be counterbalanced by means of a weight in a scale pan attached to the opposite end of a balance bar from which hangs the inner coil (Fig. 5). From the difference in the weights required to balance the suspended part on reversing

¹ Lord Rayleigh and Mrs. Sidgwick, *Phil. Trans. (A)*, **175** (1884), 411.

the current through the fixed coil, twice the value of the force of attraction is obtained. The value for the force is then independent of the action on the suspended coil of any other part of the circuit or of terrestrial or other permanent magnetism. With this arrangement Rayleigh was able to calibrate a galvanometer on the absolute scale, for, from the radii of the coils, the force produced by unit current could be calculated. The calibrated galvanometer was used to measure the current flowing in the deposition experiments, and subsequent measurements of the quantity of current could then be read off directly from the coulometer readings. The value obtained by Richards for the absolute

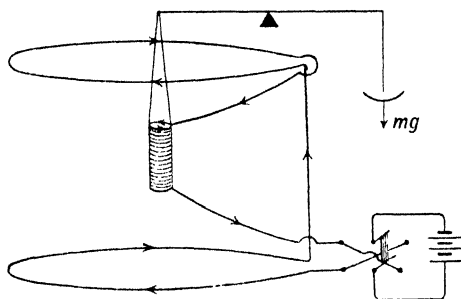


FIG. 5.—DETERMINATION OF THE ABSOLUTE UNIT OF CURRENT.

unit quantity of electricity was that quantity which deposited 0.0011172 gm. of silver. This figure was reproducible in his experiments to 1 part in 10,000, and the result may be compared with the figure 0.00111794 given by Rayleigh, who took no other precautions than to wrap the anode in a filter-paper bag.¹

For practical purposes the international unit of current is used. This quantity is fixed by convention and is independent of the precision measurements which from time to time slightly alter the accepted value of the absolute unit. It is defined as the unvarying current which deposits silver at the rate 0.0011180 gm. per second with a current density of 0.10 ampère per sq. cm. of electrode, when it is passed through an aqueous solution of silver nitrate between

¹ Lord Rayleigh and Mrs. Sidgwick, *Phil. Trans. (A)*, 175 (1884), 439.

15° and 20° C., which is used once only, and in which not more than one-third of the silver has been deposited. This unit, the ampère, is very nearly equal to one-tenth of the electromagnetic unit. In order to calculate the values of the other two units—those of resistance and E.M.F.—it is only necessary to measure one of them directly, since the other may then be deduced from Ohm's law, using the value of the unit of current.

The Iodine Coulometer.

Washburn and Bates¹ have criticised Richards' silver coulometer as a precision instrument on the ground that all the following conditions must be fulfilled before the highest degree of accuracy is assured :

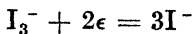
(1) A large volume of silver nitrate solution must be used and it must be very pure and quite free from dissolved air.

(2) An electroplated anode is required which should be surrounded by two porous pots.

(3) Electrolysis must be carried out *in vacuo*.

(4) The deposited silver must be fused to exclude water and silver nitrate.

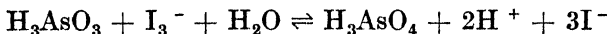
The silver coulometer is therefore by no means a convenient precision instrument, and Washburn and Bates suggest that it should be replaced by an iodine coulometer which easily gives reproducible and quite accurate results. The principle used here is the electrolysis of a solution of iodine in potassium iodide. The primary reaction which occurs is :



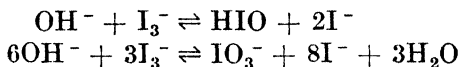
which takes place from left to right at the cathode and in the reverse direction at the anode. The amount of free iodine in the whole solution therefore remains constant, and equal amounts of the I_3^- ion disappear and reappear at the cathode and anode respectively. The amount of free iodine must be determined to an accuracy of 0.001% if the instrument is to rival the accuracy of the silver coulometer. Now, an

¹ Washburn and Bates, *J. Amer. Chem. Soc.*, **34** (1912), 1341, 1368.

accurate estimation of the liberated iodine is possible using arsenious acid :



This reaction can be made to proceed towards the right as completely as is desired, by keeping the hydrogen-ion concentration sufficiently low. If, however, it is too small, the reactions



become appreciable and interfere with the results. A buffer solution of sodium phosphate is therefore used. In this way the hydrogen-ion concentration is maintained sensibly constant despite disturbing influences such as the presence of small quantities of alkali. The mixture of disodium hydrogen phosphate and sodium dihydrogen phosphate in the buffer is chosen in such proportions that at the end of the reaction the hydrogen-ion concentration is just equal to that of pure water.

The coulometer consists of twin upright limbs connected by a V-tube and platinum-iridium electrodes are fused through the lower ends of these vessels (Fig. 6). When the electrodes are in position the whole instrument is filled by means of the side tubes with a 10% solution of potassium iodide. Concentrated potassium iodide solution and a saturated solution of iodine in potassium iodide are introduced respectively at the anode and cathode, through the tap funnels. After the current has passed for the requisite time, the solutions round the two electrodes are withdrawn and analysed. As the amount of iodine formed at one side is equal to the amount which disappears at the other, the instrument is free from any constant source of error. With the silver coulometer, however, the reactions taking place at the anode are not reversible, and the reaction at the cathode

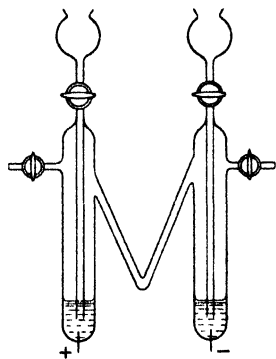


FIG. 6.—IODINE COULO-METER.

cannot be used to check that at the anode as in the reversible silver coulometer. Moreover, there is no possibility of any error in the latter due to the presence of foreign-included material, since no deposition takes place. The accuracy of the iodine coulometer is limited only by the accuracy with which the titration of the free iodine may be carried out, and there is no doubt that, compared with the Richards' type, it possesses many advantages which commend its use for ordinary work wherever possible. But in spite of its advantages for practical coulometric measurements, the iodine coulometer cannot rival the silver instrument for precision determinations, for it is not possible to undertake the titrations with a sufficiently high degree of accuracy. The silver coulometer has therefore been adopted for obtaining the best experimental value for the faraday.

The Copper Coulometer.

The copper coulometer has often been used in ordinary laboratory practice, although it cannot be used as an accurate instrument. The greatest obstacle to its use for accurate work is the fact that copper is more easily oxidised at the cathode than silver. This effect is further accentuated since the copper falls through the solution in a finely divided state, and thus presents a large surface for oxidative action. If a high current density is used, hydrogen as well as copper, is evolved at the cathode, whilst at low current densities some of the copper stays in solution as Cu^+ ions due to the reaction



The deposit weighed is, in either case, not strictly a measure of the quantity of electricity which has passed. The effects of oxidation at the cathode may be lowered by keeping the solution strongly acid and by working at low temperatures. Even so, purely chemical corrosion is not entirely eliminated, and it is a matter of extreme difficulty to determine the exact influence of the electric current on this chemical corrosive action.¹ The most reproducible results obtainable with an

¹ A critical review of the electrolysis of copper sulphate is given by G. Gore, *Nature*, **25** (1882), 473; **27** (1883), 326, 374.

ordinary copper coulometer are not consistent to better than 1 part in 300.

In an investigation of the electrochemical equivalent of copper, Richards¹ used the type of cell illustrated (Fig. 7). The formation of Cu^+ ions was minimised by carefully excluding air, keeping the solution of copper sulphate cold, and operating the cell at a low temperature. Only low current densities were used, as otherwise hydrogen was liberated from the cathode. Now, the loss of copper due to the formation of Cu^+ ions was found to be approximately proportional to the area of the electrode surface. From the curve, obtained by plotting the amount of copper deposited against the electrode surface area, the corrected value at zero surface for the amount of copper deposited could be read off at once. This was consistent with the best values for the chemical equivalent previously obtained.²

The mass deposition number³ found in this way was 0.003292 gm. per coulomb, an accuracy of 1 part in 1,000 being claimed. Whereas, therefore, the chief disturbing reactions in the silver coulometer seem to occur at the positive pole, the errors in the copper coulometer are due to a definite side reaction which takes place in the solution, and which can never be entirely eliminated even with the most careful precautions.

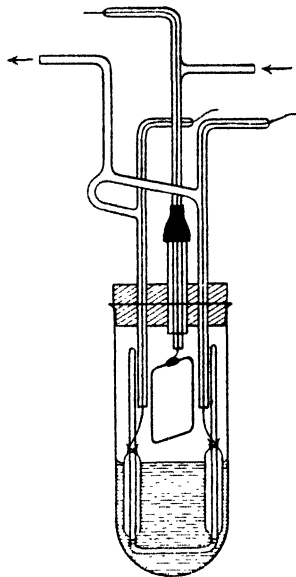


FIG. 7.—RICHARDS' COPPER CELL.

¹ Richards, Collins, and Heimrod, *Z. physikal. Chem.*, **32** (1900), 321.

² Gray, *Phil. Mag.*, **22** (v) (1886), 407; **25** (v) (1888), 179.

Shaw, *Brit. Assoc. Report* (1886), 318.

³ Not to be confused with the electrochemical equivalent (see p. 35).

The Sodium Coulometer.

The sodium coulometer is especially to be recommended for use under ordinary experimental conditions, where a high degree of reproducibility is required together with ease of manipulation. Its operation depends on a principle first discovered by Burt.¹ If an ordinary incandescent filament lamp be lowered into molten sodium nitrate, the electrons emitted from the filament neutralise the sodium ions in the glass and fresh ions from the molten salt pass into the glass to replace these. The soft glass of the bulb is quite a good conductor at the melting point

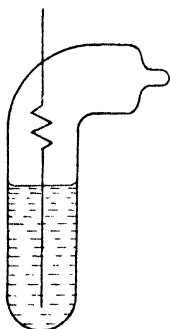


FIG. 8.—
THE SODIUM
COULOMETER.

of sodium nitrate, and electrodeposition of the sodium on the inner surface of the glass proceeds, therefore, so long as the filament is kept hot. If a sodium-amalgam-in-glass electrode is used in place of lamp-bulbs, the quantity of sodium which passes through the glass may be estimated by titration of the total alkali against standard acid.² Mercury is not a good amalgamator and the mercury amalgam is best replaced by an alloy of sodium in cadmium. This is placed inside soft lime-glass electrodes and connection is made by a fused-in platinum wire (Fig. 8). These electrodes are weighed

accurately and suspended in a bath of molten sodium nitrate kept at 340° C. The increase in weight due to the passage of sodium through the glass then gives an accurate measure of the quantity of electricity which has been passed. Anode results are found by estimating the quantity of sodium inside the vessels before and after the passage of the current, instead of noting the change in weight of the bath. These are in very close accord with results obtained by using the silver coulometer. Small cathode errors arise from the electrolytic loss of silicate ions from the cathode surface of the glass. Used anodically, the instru-

¹ R. Burt, *Physical Rev.*, **27** (1926), 813; *J. Opt. Soc. Amer.*, **11** (1925), 87.

² O. J. Stewart, *J. Amer. Chem. Soc.*, **53** (1931), 3366.

ment is capable of an accuracy of 1 part in 10,000, comparing very favourably with the best results of the silver coulometer. The silver coulometer is, however, still used as the precision instrument, and the best experimental value of the faraday has been obtained from determinations made with it.¹

Precision Determinations of the Faraday.

Considerable confusion has arisen from time to time over the exact distinction between the electrochemical equivalent and the mass of material deposited per unit quantity of electricity passing. The value of the electrochemical equivalent of an element like the faraday is regarded as a universal constant, whereas the mass of material deposited per unit quantity of electricity may be affected by the experimental conditions. Measurements made with the silver and iodine coulometers show a discrepancy of 32 parts in 10^5 , which must be due to the fact that in either or both of these the measured deposit does not represent the true mass carried by the given quantities of electricity.² A careful investigation of the errors accompanying the silver coulometer show that the only serious constant error is one of about 1 part in 2,000, provided a proper design of instrument is used with a due consideration for the precautions already mentioned. This has been traced to the inclusions of foreign matter in the weighed deposit, together with a possible further and very small error, due to parasitic chemical reactions taking place in the solution.³ It must therefore be supposed that the discrepancy between the iodine and the silver coulometers is due to errors in the former. The results obtained from the deposition of silver have therefore been used in choosing the international value of the faraday, which has been fixed at 9,648.9 in absolute electromagnetic units. This value is obtained from the best values for the atomic weight of silver, 107.880, and for its electrochemical equivalent, 0.0111805.

¹ R. T. Birge, *Rev. Mod. Phys.*, **1** (1929), 1.

² E. W. Vinal and S. J. Bates, *Bull. Bureau Standards*, **10** (1914), 424.

³ E. W. Vinal and W. M. Bovard, *ibid.*, **13** (1916), 147.

Not only is this constant of the utmost importance in electrochemistry, but the accuracy with which it can be found experimentally is a contributing factor in determining the accuracy of the experimental value of Avogadro's constant. These universal constants are related by the equation

$$N = Fe \quad . \quad . \quad . \quad . \quad (12)$$

where e is the charge on the electron which may be determined accurately by Millikan's balanced oil-drop method.¹ The best mean value which has been obtained for e is $(0.4770 \pm 0.005) \times 10^{-10}$ e.s.u.,² so that, expressing e in electromagnetic units by multiplying its value in electrostatic units by $(2.99796 \pm 0.00004) \times 10^{-10}$ cm.-sec⁻¹, the value of N from these constants is $(6.059 \pm 0.006) \times 10^{23}$. Now, since both F and e are, by agreement, fixed constants independent of the conditions, so also will be the value obtained in this way for N , whereas in reference to its true meaning in the theory of gases it will vary with the gas, for at N.T.P. no two gases behave kinetically in exactly the same manner.

The Measurement of Potential Difference.

Now, we have seen that there are two methods of studying solutions of electrolytes. The type of measurements which we have been considering are related to irreversible processes in electrolytes. On the other hand, we associate Lewis's activity with the reversible processes like the osmotic properties of electrolytes. The activity of a solution of an electrolyte at a given concentration may be determined from the E.M.F. of a galvanic cell which contains the solution between two reversible electrodes. Unfortunately, unless very special precautions are taken, the E.M.F. of a galvanic cell is rarely reproducible to less than one-tenth of a millivolt and measurements are not usually made to an accuracy exceeding this figure.

The principle upon which almost all the measurements of potential difference are based was first used by Poggendorff

¹ R. Millikan, *Phil. Mag.*, **34** (vi) (1917), 12.

² R. T. Birge, *Rev. Mod. Phys.*, **1** (1929), 36.

in his compensation method (Fig. 9). It depends on calibrating, with a standard E.M.F., the potential drop from a steady source along a uniform wire resistance. Equal lengths of this will then correspond to equal decrements of potential, and a length may be tapped off along which the potential fall is exactly equal to that of the unknown E.M.F. If the two potential differences are opposed, they may be balanced by observing when a galvanometer in the circuit registers no current. In this way the errors which always arise from direct readings are avoided and the conditions are as nearly as possible truly reversible, thus ensuring thermodynamic equilibrium. As a constant source of potential fall along the resistance, a 2-volt accumulator, half run down, may be most conveniently used. The potential drop per unit length of the resistance wire due to this may be calibrated by using, in place of the experimental cell, a standard cell, the E.M.F. of which is known with accuracy at any particular temperature (Fig. 9). The potential difference between the ends of the wire need not be known, since the accumulator is required only to provide a steady and constant potential difference between the ends of the wire, and the standardisation of this has been effected by the use of the standard cell.

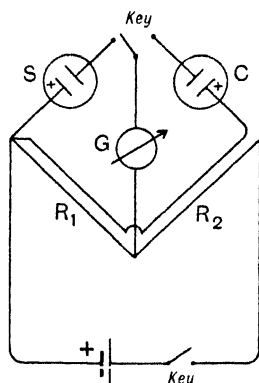


FIG. 9. — COMPENSATION METHOD FOR DETERMINING E.M.F.

Now, a simple potentiometer wire, even if it is extended in length by the addition of wire to each end of the actual slide-wire, can never be read to a high degree of accuracy, and lack of uniformity in the wire may lead to minor errors. Reliable and compact slide-wire potentiometers have therefore been designed for more accurate measurements. In these the slide-wire is replaced by a coil R_1 (Fig. 10) of low resistance arranged in a circle and read by a slide, operating on a dial which is divided into definite fractions of a millivolt. Connected to one end of this slide-wire are a number

of coils R_2 of the same resistance, any number of which may be tapped off, thus extending the effective length of the wire to many times its divided length. The standard cell may be arranged to be connected across a definite resistance of the potentiometer circuit such that, when no current flows through the galvanometer, each potential coil is made to correspond to a potential fall of 0.1 volt. The setting for the cell of which the E.M.F. is required, is not disturbed by such an adjustment of the coils. In order to avoid changes in the resistance of the coils and the slide-wire due to variations of temperature, these are constructed of manganin, which has a very low temperature-coefficient

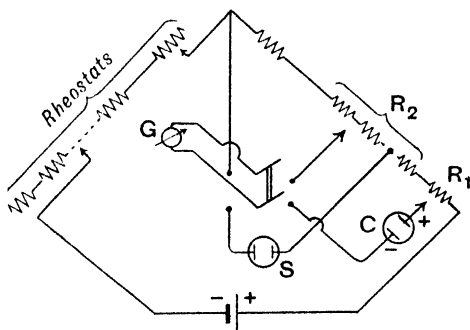


FIG. 10.—SLIDE-WIRE POTENTIOMETER. (Cambridge Instrument Co.)

of resistance. For ordinary laboratory measurements a more accurate potentiometer may be constructed from resistance boxes by connecting two of these in series through a 1-ohm variable rheostat and using the moving arm of the rheostat as the "jockey" of the potentiometer. If the resistance in the galvanometer circuit required to balance the standard cell be R_s , and that required to balance the cell the E.M.F. of which it is required to determine, be R_c then,

$$\frac{\text{E.M.F. of cell to be measured}}{\text{E.M.F. of standard cell}} = \frac{R_c}{R_s} \quad (13)$$

The limit of accuracy of these methods is fixed by the sensitivity of the galvanometer and the resistance of the cell circuit. Usually a laboratory galvanometer of the sus-

pended coil type gives a deflection of the order of 500 mm. at 1 metre distance, for a current of 1 milliampère. Now, assuming that it is possible to read the scale to half a millimetre, the galvanometer will therefore record 10^{-9} ampère. The resistance of the cell is fairly certain in ordinary work to be small compared with that of the resistance coils in the potentiometer, and the total resistance of the cell circuit may be taken to be of the order 10^4 ohms. The smallest unbalanced E.M.F., therefore, which can be detected will be about $10^{-9} \times 10^4 = 10^{-5}$ volt. So high a degree of accuracy is not usually required, since it is a difficult matter to maintain the E.M.F. of any cell reproducible within these limits.

In most of the early methods for measuring potential differences a capillary electrometer was used in place of a galvanometer as a current detector.¹ The operation of this instrument (Fig. 11) depends on the fact that the surface tension of mercury varies with the charge residing on its surface—*i.e.*, that the surface tension at a mercury-liquid interface depends on the potential difference across the surface. The change in surface tension may be observed by the variation in the height of the interface contained in a very narrow capillary tube. The slightest movement of the mercury in either direction may be detected by observing the interface through a measuring microscope, and it is possible to measure differences in potential as small as 1 millivolt. The passage of a current for any length of time, however, causes electrolysis to take place, accompanied by the deposition of mercurous sulphate. The instrument is therefore kept short circuited when the measurement is not actually being made. A further source of error in Lippmann's electrometer arises from the tendency of the solution to creep down between the mercury column and the

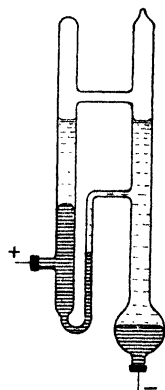


FIG. 11.—THE CAPILLARY ELECTROMETER.

¹ Lippmann, *Ann. Physik*, **79** (1875), 494; *Pogg. Annalen*, **149** (1873), 547.

glass. This may often result in a considerable alteration in the magnitude of the phase boundary exposed to the potential difference, and very erroneous values for the E.M.F. may thus be recorded.¹ These errors reduce its accuracy far below that attainable with a galvanometer circuit and it has now been entirely discarded in favour of the latter for all practical work.

For many purposes it is necessary to determine the E.M.F. of a cell the resistance of which is very high. The current through the galvanometer in the Poggendorff circuit would in this case be so small that the instrument would be rendered insensitive. In many cases also the system for which the E.M.F. is required may be very easily polarised, and the exact conditions under which the potential is required would then be disturbed even by a small current drawn from the cell while finding the balance point. In these cases the ordinary Poggendorff compensation method may be used in conjunction with a Lindemann-Keeley electrometer² as a current detector for observing the balance point. This instrument has a very low capacity, and is therefore very sensitive to small currents. It consists of a needle supported centrally at the mid-point of a quartz platinised fibre held under tension so that it may rotate between four crossed plates. The electrometer plates are charged from a high-tension battery, and the movement of the needle, which is observed in a microscope, is then determined by the current passing down the fibre. The sensitivity of the instrument depends on the tension of the fibre. The apparatus has a stable zero and requires no levelling, although, in order to ensure that the electrical and mechanical zeros coincide, it is necessary to adjust the charges on each pair of plates rather accurately by connecting them to two small potentiometers.³

¹ Practical details of an accurate capillary electrometer and an account of the precautions which must be taken to obtain reproducible readings are given by K. O. Koenig, *Z. physikal. Chem.* (A), **154** (1931), 454.

² F. A. Lindemann and T. C. Keeley, *Phil. Mag.*, **47** (vi) (1924), 577.

³ Mrs. P. T. Kerridge, *J. Sci. Instr.*, **3** (1926), 404.

Thermionic Valve Potentiometers.

A method which has found considerable favour for measuring the potential differences in cell circuits of very high resistance depends on the characteristics of the thermionic valve. The ordinary type of wireless valve is for this purpose replaced by a low-capacity "soft" electrometer valve designed to eliminate the disturbing effects which may arise from the formation of positive ions from the residual gas in the valve. The principle of operation is, however, the same with either type of valve. The electrons emitted by the heated filament are attracted to a positively-charged plate (the anode), and in their passage from filament to plate they pass through a grid, the potential of which may be varied with respect to the filament. The grid may, by virtue of its potential, exert a very great attractive force on the electrons, but when they reach it their velocity is so great that they suffer only a slight deviation from their path and almost all of them reach the anode. Thus the current in the anode circuit is determined mainly by the magnitude of the grid potential, provided the potential on the plate is kept constant. The magnitude of the anode current is also directly proportional to the potential V_a on the plate when the grid potential V_g is kept constant so that for a large range on either side of $V_g = 0$ the current in the anode circuit may be represented by the equation,

$$i_a = \text{constant} + K_1 V_g + K_2 V_a \quad . \quad . \quad (14)$$

In this equation the influence of the second term is usually much greater than that of the last, and the maximum value of the ratio $\frac{K_1}{K_2}$ is defined as the amplification factor of the valve. A set of triode characteristics for different values of V_a , showing the steep, straight portions of the curve to which the above equation applies, are plotted in Fig. 12. Modern valves are designed to make the rising sections of the curve as straight as possible.

Now, if a triode is to be used for measuring an unknown potential which is applied between the grid and filament, the

constant and the term $K_2 V_a$ in the equation for i_a must be balanced out by means of an accumulator and a variable resistance (Fig. 13).¹ The deflection recorded on a sensitive galvanometer will then be directly proportional to the applied E.M.F. in the grid circuit. Since the current

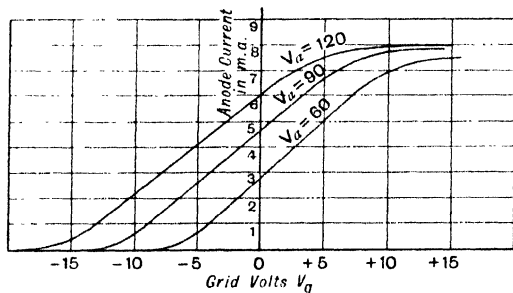


FIG. 12.—VALVE ANODE CHARACTERISTICS.

through the grid circuit is practically zero, due to the high total impedance (internal resistance) of the valve, readings may be taken continuously without using a tapping key. The arrangement has to be calibrated by making measurements with a standardised potentiometer.

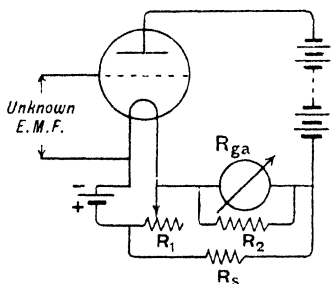


FIG. 13.—SIMPLE VALVE POTENTIOMETER (Goode).

The accuracy of this method of measuring potential differences is much improved by modifying the circuit so that it may be used as a null method,² since any variations in the filament emission or in the plate potential can then be balanced out by backing one valve against another. If two valves of high amplification factors and mutual conductances

are exactly matched in regard to their anode characteristics and are connected in parallel, they will detect

¹ Goode, *J. Amer. Chem. Soc.*, **47** (1925), 2483; **44** (1922), 26. For valve potentiometers using the charge and discharge of a condenser, see C. Morton, *J.C.S.* (1931), 2977; Beans and Oates, *J. Amer. Chem. Soc.*, **42** (1920), 2116.

² Compton and Haring, *Trans. Amer. Elect. Soc.*, **62** (1932), 345.

in the anode circuit any small difference between the potentials of the two grids with respect to their filaments. The circuit illustrated in principle in Fig. 14 would therefore serve very well as a differential valve potentiometer. One modification in the simple circuit must, however, be introduced to allow for the fact that no two valves can be obtained which have exactly the same anode currents for the same grid potentials. As the potentials in the grid circuits are being opposed at the balance point (the unknown E.M.F. against a tapped-off E.M.F. from a standardised potentiometer), the valve characteristics are being employed only for very small variations in grid potential. If therefore the characteristics for the two valves can be made to coincide over the small range of grid potentials used, the required conditions will be satisfied. Now, a variation in the filament current of one of the valves will influence the anode current of that valve, and in this way may be used to bring the two char-

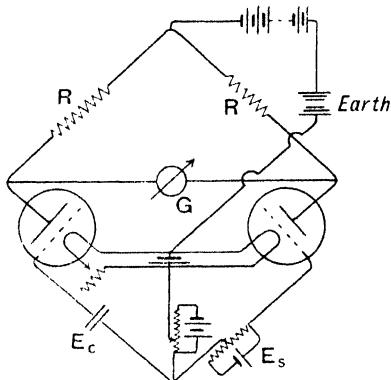


FIG. 14.—DIFFERENTIAL VALVE POTENTIOMETER.

acteristics together over the operating range. The adjustment of the filament current is made with two equal potential differences in the grid circuits, each tapped off from a potentiometer and each approximately equal to the E.M.F. being measured. The potential difference required is then put into one grid circuit and a standardised potentiometer opposed to it in the other. It is, of course, necessary to shield the valves carefully in earthed screens in order to prevent the grids from picking up any stray charges.

In order to obtain the highest sensitivity $\frac{\partial i_{ga}}{\partial E}$ where i_{ga} is the galvanometer current and E is the unbalanced potential

in the grid circuit, it is necessary to choose the operating grid voltage rather carefully. The grid potential at which the slope of the anode characteristic is a maximum may be defined as the critical grid potential. Its value varies with the applied plate voltage, but the values of the critical grid potential and the plate voltage which, together, give the maximum positive slope of the anode characteristic (maximum "effective" mutual conductance), will be the conditions most suitable for high sensitivity. It may easily be shown from a consideration of the single-stage circuit¹ shown in Fig. 13 that, provided the galvanometer has a low resistance and the values of the resistances R_s are high—

i.e., $\frac{R_s}{R_s + R_{ga}}$ is approximately unity, so that a large fraction of the total anode current passes through the galvanometer—provided also the valves have a high anode impedance, then the sensitivity of the circuit is given very approximately by

$$\frac{\partial i_{ga}}{\partial E} = \frac{R_g G}{R + R_g} \quad . \quad . \quad . \quad (15)$$

Here R_g is the grid impedance of the valves, G the normal mutual conductance, and R the internal resistance of the source of measured potential difference. It follows that, for a cell of high internal resistance, a maximum sensitivity G will be obtained when $R_g = -R$. Using valves of high mutual conductance and high insulation, it is quite easy to measure an unbalanced potential of 10^{-5} volt using a galvanometer of sensitivity 10^{-9} ampère per division and the zero drift is far too small compared with the observed deflections on the galvanometer to introduce any appreciable error during the time required for a determination. Moreover, the sensitivity remains practically unaltered when the unbalanced E.M.F. is in a circuit of very high resistance. A potentiometer of this design is therefore much more sensitive than a Lindemann electrometer used as a potential measuring device, whilst it retains the general stability which characterises the latter.

¹ C. Morton, *J.C.S.* (1931), 2983.

Sources of a Steady Potential Difference.

Now, there are two conditions which must be observed in every potentiometric measurement if a high degree of accuracy is to be attained. One is the maintenance of a perfectly steady and constant potential drop between the ends of the potentiometer resistance. The other is the use, for calibrating the potentiometer, of a cell the E.M.F. of which is known with complete certainty under the conditions of the experiment. The most convenient source of a uniform and constant potential drop between the ends of a potentiometer resistance is a half-run-down accumulator. Before this reaches its discharged state it supplies a very steady

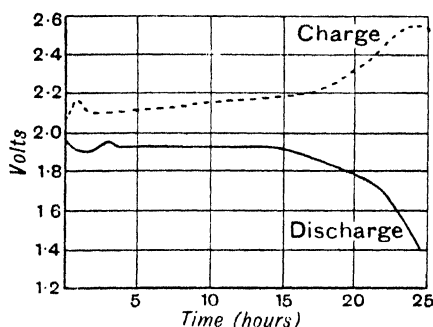


FIG. 15.—CHARGE AND DISCHARGE OF AN ACCUMULATOR.

potential difference over a certain range of its discharge (see Fig. 15). Now, an accumulator, even when run down, always tends to recover to the initial E.M.F. on standing. It is therefore very necessary always to allow it to discharge for a short time until it reaches its steady value, before measurements are actually made. Instead of an accumulator a Hulett cell

$\text{Cd} : \text{Hg (two phase)} | \text{CdSO}_4(\text{conc. solution}) |$

$\text{Hg}_2\text{SO}_4 : \text{Hg (two phase) with 1\% H}_2\text{SO}_4$

may be used as a source of steady E.M.F. for the potentiometer resistance.

The Standard Cell.

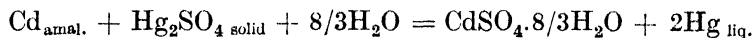
The standard cell with which the potentiometer coils are standardised has to conform to a number of conditions,

for on the accuracy of its reproducibility depends that of the results which are obtained for the E.M.F. of the unknown cell. Besides being easily reproducible, it is essential that it should have only a very small temperature coefficient. The Clark cell was at one time very widely used, but it has been rejected in favour of the cadmium cell, owing to its very high temperature-coefficient of E.M.F. A further condition to which the standard cell must conform is a small temperature lag, so that the cell recovers quickly from a temperature change. It must also recover rapidly from changes in E.M.F. due to polarisation (an irreversible process which occurs at the electrodes in many cells when any appreciable current is passed). Finally the standard cell should possess chemical stability, so that it may be used over and over again without any adjustment of any kind.

Practically the only cell which fulfils all these conditions, and the only one now used at all generally, is the Weston cell.¹ Obviously the condition of chemical stability excludes immediately all two liquid cells which depend for their action on the diffusion of ions through a porous membrane. In the Weston cell the cell liquid is cadmium sulphate solution. This solution may be saturated or at some other definite concentration, the cell being described respectively as the "saturated" or "unsaturated" cadmium cell. Only the saturated form



is in general use, and the cell reaction taking place here may be represented by the equation



The electrodes consist of an amalgam of cadmium and mercury containing 12.5% of cadmium as a cathode and a paste of mercurous sulphate and mercury as a depolariser above a layer of mercury which constitutes the anode. The choice of an alloy containing 12.5% of cadmium for the cathode may appear somewhat arbitrary, but if the E.M.F.

¹ Wolff and Waters, *Bull. Bureau Standards*, 4 (1907-1908), 1, 18. Full details for the preparation of a Weston cell and for the purification of the materials are given here.

of the cell be plotted as a function of the composition of the amalgam, it is found that the E.M.F. changes only very slightly over the range 10–15%, but that it rises quite rapidly up to 10% and above 15% amalgam. Any changes

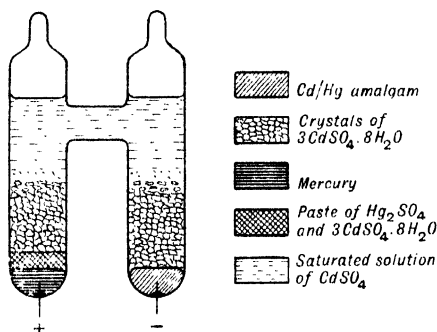


FIG. 16.—WESTON CELL.

in the composition of the amalgam in either direction will therefore have the least possible effect on the value of the E.M.F. when the amalgam contains initially 12·5% of cadmium. The alloy may be prepared simply by warming together the two components in the correct proportions in a test-tube.

One of the most important conditions which has to be observed in the construction of the cell is the complete purity of the mercurous salt. It is best prepared, like all mercurous salts, by making mercury the anode in a solution of sulphuric acid electrolysed with an inert cathode. If some device is used to keep both the mercury and the solution stirred, a fresh surface is continually exposed to the solution and the mercurous salt formed by the interaction of the metal with discharged SO_4^{--} ions accumulates on the surface of the mercury.¹ This mercurous

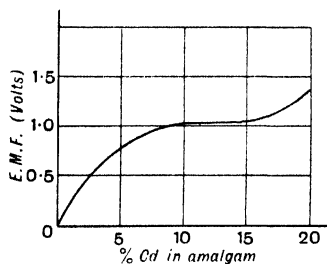


FIG. 17.—VARIATION OF E.M.F. OF WESTON CELL WITH COMPOSITION (DIAGRAMMATIC).

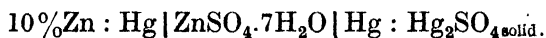
¹ F. A. Wolff, *Trans. Amer. Elect. Soc.*, 5 (1904), 49.

chloride, made into a paste with more mercury, to ensure the complete absence of mercuric salt, is placed over the mercury anode of the cell.

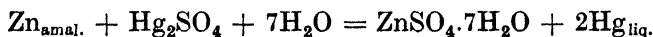
Precautions have to be taken during the preparation of the cadmium sulphate solution to heat the solution only very gently, for at 74° C. the hydrate $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ changes into a new and stable solid phase, $\text{CdSO}_4 \cdot \text{H}_2\text{O}$. If a solution which is saturated with cadmium sulphate be used at 4° C. the changes in concentration with temperature are eliminated, but as cadmium sulphate has a very small temperature coefficient of solubility, the advantage to be gained by working at 4° C. is hardly sufficient to justify the inconvenience caused by it. The solution is therefore usually kept saturated at all temperatures by introducing a layer of fine crystals of $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ over the cadmium amalgam on the cathode side. The E.M.F. of the cell at 18° C. is 1.0183 volts, and as the temperature coefficients of the separate electrodes are almost exactly equal and opposite, the net temperature coefficient is very small, of the order -0.00004 volt per degree. The E.M.F. at any other temperature may be obtained from the equation

$$E_T = E_{20} - 0.0000406(T - 20) - 0.0_695(T - 20)^2 - 0.0_91(T - 20)^3 \quad . \quad . \quad (15)$$

The Clark cell ¹ is the only other standard cell of importance, but it has been almost entirely replaced by the cadmium cell owing to its large temperature coefficient. It is, in principle, exactly similar to the cadmium cell, except that the cadmium is replaced by a 10% amalgam of zinc in mercury and a saturated solution of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ is used as the cell solution :



The cell reaction is



and its E.M.F. is given by the expression

$$E_T = 1.4330 [1 - 0.0084 (T - 15)] \quad . \quad . \quad (16)$$

¹ Clark, *J. Soc. Tel. Eng.*, 1 (1878), 53.

We have now considered the important fundamental measurements which will be needed in our discussion of the properties of electrolytes in solution. It has been emphasised that electrochemical measurements may be considered to fall into two groups, according as they concern the irreversible processes which may be made to take place in the solution, or the thermodynamic properties. And it is not only in a consideration of the experimental work that this subdivision is made clear, but the same distinction must be drawn in the theoretical treatment of electrolytic properties. In the theoretical consideration of irreversible processes, where the electrolyte is in mass motion, the laws of hydrodynamics must be applied to the ion atmosphere theory, but with the thermodynamic reversible properties a calculation of the free energy of the solution will enable all the properties to be determined.

CHAPTER III

THE CONDUCTIVITIES OF SOLUTIONS

The General Theory of Conductivity.

It will be remembered that Kohlrausch showed that, in dilute solutions, the conductivities of strong electrolytes could be expressed empirically by the equation (1) :

$$\Lambda = \Lambda_{\infty} - k\sqrt{c}$$

This equation may, however, be obtained from the ion atmosphere theory. Moreover, the reason why it applies only to the limiting case of very dilute solutions is apparent from the assumptions which must be made in deducing it. Debye and Hückel first showed that, as a consequence of the ion atmosphere which forms round any ion, this ion is subject to two retarding influences when it moves in an electric field.¹ First, as the central ion moves forward, the centre of its atmosphere lags a little behind it, and therefore, because it has predominantly a charge of the opposite sign, it tends to pull the ion back. This is called the disymmetry effect. Also, since each ion is solvated (see Chapter XI), the central ion will be moving in a region where, relative to it, the solvent associated with the ions of its atmosphere is drifting in the opposite direction. This is called the electrophoretic effect, and it will still further slow up the motion of the ion.

Now, the magnitude of the disymmetry effect is measured indirectly in terms of the "time of relaxation" of the ion atmosphere. The value of this may be obtained as follows. The potential at the central ion, due to the ion atmosphere

¹ Debye and Hückel, *Physikal. Z.*, **24** (1923), 305.

alone, has been calculated by Debye and Hückel ¹ (equation 269) to be

$$\psi_{II} = \frac{z_i e \kappa}{D}$$

z_i is here the valency of the central ion, D is the dielectric constant, and κ is defined below. This expression is equal to the potential which would be set up by z_i electrons each carrying a charge e and situated at a distance $1/\kappa$ from the central ion. The distance $1/\kappa$ is therefore known as the thickness of the ion atmosphere, and its value for the general case is given by equation (272),

$$\kappa = \sqrt{\frac{4\pi e^2}{DkT} \sum n_i^2 z_i^2}$$

n_i being the number of ions of the type i present in the solution. Now, if an ion is removed to infinite distance from its surrounding electrolyte, its ion atmosphere will disappear. The time interval required for the ions to return to a random distribution is called the time of relaxation τ of the ion atmosphere. It is equal to the time required to build the ion atmosphere up again when the ion is returned to the solution in the absence of any external field. Now, it may be shown from a consideration of the conditions which must be observed in order to solve the general hydrodynamical equations in the special case of electrical conductivity ¹ that τ is given by the equation,

$$\tau = \frac{\rho}{2\kappa^2 kT} \quad . \quad . \quad . \quad . \quad (17)$$

where ρ , the "frictional coefficient" of the ions, depends on the mobility and is equal to $\frac{1.5 \times 10^{-7}}{\text{mobility}}$. For aqueous solutions of potassium chloride the time of relaxation becomes $\frac{1}{\gamma} (0.55 \times 10^{-10})$ second, where γ is the equivalent concentration. This is of the same order of magnitude as that of other similar molecular or atomic processes; *e.g.*, the time of relaxation of polar molecules in an alternating field is of the order 0.25×10^{-10} second.

¹ Debye and Hückel, *Physikal. Z.*, **24** (1923), 185.

We see therefore that, due to both the disymmetry and the electrophoretic effects of an ion atmosphere, the mobility of an ion is lowered. Moreover, the greater the concentration of the solution the greater will be the lowering of the mobility, since there will be more ions present in the ion atmosphere.

The consequences of interionic attraction include two further interesting effects in connection with conductivity properties. If the frequency of an alternating electric field applied to the electrolyte be very great compared with the time of relaxation, the ion atmosphere will never have time to re-form round the central ion, and there will be no disymmetry effect at all. There should therefore be a dispersion of the conductivity with the frequency.

Further, with very large fields the velocities of the ions become so great that, during the time of relaxation, an ion moves through a distance many times greater than the thickness of the ion atmosphere, and both the disymmetry and the electrophoretic effects disappear. For high fields, therefore, there should again be a dispersion effect on the conductivity, as with rapidly alternating fields. Both those effects have been observed (see pp. 104-9), and since neither could be explained in terms of the Arrhenius dissociation theory, they constitute a very important piece of evidence in support of the ion atmosphere theory.

Debye and Hückel worked out the general equations for non-stationary processes in dilute solutions of strong electrolytes by an application of the ordinary laws of hydrodynamics.¹ Consider the motion of an ion through the solution under an electric field when it has a constant velocity V . Now, arising from the disymmetry effect, this ion will be subject to an additional field intensity ΔX_i , which will be in a direction opposite to the mean velocity of the central ion. Its magnitude with an ion of the i th type is calculated by Debye and Hückel to be

$$\Delta X_i = - \frac{300 e z_i}{6} \frac{\kappa}{D} \frac{1}{kT} \rho_m u_i \quad . \quad . \quad (18)$$

¹ Debye and Hückel, *Physikal. Z.*, **24** (1913), 305.

Debye, *Trans. Faraday Soc.*, **23** (1927), 334.

In this equation u_i , the velocity in cm. per sec. of an ion of type i and valency z_i , may be expressed in terms of the mobility v_i and X the applied field,

$$u_i = v_i X = \frac{ez_i}{\rho_i} \cdot \frac{300}{X}$$

$$\text{i.e.,} \quad \Delta X_i = - \frac{1}{6} \frac{z_i^2 e^2}{D} \cdot \frac{\kappa}{kT} \cdot \frac{\rho_m}{\rho_i} \cdot X \quad . \quad . \quad (19)$$

ρ_i is the frictional constant for an ion of the i th type, whilst ρ_m is the mean frictional coefficient for all the ions of the electrolyte. Only when all the ionic species have equal velocities will

$$\rho_m = \frac{\sum_s u_i z_i^2 e^2 \rho_i}{\sum_s u_i z_i^2 e^2} = \rho_i$$

In order to calculate the electrophoretic effect Stokes' law is used. According to Stokes' law, the frictional force R is given by

$$R_i = 6\pi\eta r_i u_i \quad . \quad . \quad . \quad . \quad (20)$$

where r_i is the radius of the particle moving with velocity u_i and η is the internal viscosity of the liquid. In the case of a charged ion moving through the solution with its ion atmosphere, under an external field X , this field will act upon the charges constituting the atmosphere, in a manner for which Stokes' law makes no allowance. The calculation of the consequent additional frictional force ΔR_i may, however, be made in a manner similar to that adopted by Helmholtz in his theory of electrophoresis, if it is assumed that the ordinary macroscopic laws of hydrodynamics apply at a distance of a few molecular diameters.

The apparent charge located in the ion atmosphere in concentric shells of thickness dr round the central ion, can be computed by means of equation (269) for the potential due to the ion atmosphere. The total effect of the ion atmosphere on the frictional force may then be found by applying Stokes' law to each of these shells and integrating over the whole atmosphere. Debye and Hückel showed by

such a calculation that there is an increase ΔR_i in the apparent frictional force, given by

$$\Delta R_i = z_i e X r_{i\kappa} \quad . \quad . \quad . \quad (21)$$

Both the effects of the ion atmosphere on the motion of the ion have now been calculated. When the ion is moving with its equilibrium velocity, the whole electric force $ez_i(X - \Delta X_i)$ must be equal to the total frictional force—i.e., from (19), (20) and (21),

$$ez(X - \Delta X_i) = \\ ez_i X - \frac{300}{6} \frac{e^2 z_i^2}{D} \frac{\kappa}{kT} \rho \eta_m V_i X + 6\pi\eta v_i r_i X + z_i e X r_{i\kappa} \quad (22)$$

or

$$V_i = \frac{ez_i X}{6\pi\eta r_i} \left[1 - r_{i\kappa} - \frac{\rho_m}{6\pi\eta v_i} \cdot \frac{e^2 z_i^2 \kappa}{6DkT} \right] \quad (23)$$

This equation for the mobility of an ion, obtained by Debye and Hückel, shows that the correction for the mobility is proportional to κ and hence (equation 272) to the square root of the concentration. The deduction of equation (23) therefore gives a theoretical explanation of Kohlrausch's law.

Onsager's Modifications in the General Theory of Conductivity.

Onsager has, however, pointed out an important omission in Debye and Hückel's calculations.¹ They supposed the ion to follow a straight path through the solution while under the influence of the applied field. Now, due to the thermal agitation of the ions around it, it will follow, not a straight course, but a zigzag one, and this will influence the ion atmosphere, and therefore its effect on the central ion. The calculations of Debye and Hückel therefore give too high a value for the additional effects due to the charges in the ion atmosphere. Moreover, due to the diffusion of two ions in relation to one another, there is a combined relaxation effect of both the ion atmospheres which must be taken into account. To allow for this, another term must be introduced in the equation for the additional electric field caused by

¹ Onsager, *Physikal. Z.*, 28 (1927), 388.

the atmosphere. By taking these effects into account, Onsager showed that the potential round a moving ion was only a very little different from that round a stationary ion. The retarding field effect ΔX_i due to the ion atmosphere on an ion of the i th type in a dilute solution of an electrolyte with only two types of ions, was given by Onsager as :

$$\Delta X_i = \frac{e^2 z^2}{3DkT} \cdot \frac{\kappa_1^2}{\kappa + \kappa_1} \cdot X \quad . \quad . \quad . \quad (24)$$

Here κ is the Debye-Hückel factor defined by equation (183)

$$\kappa^2 = \frac{4\pi e^2}{DkT} \cdot \frac{N}{1000} \cdot (u_i z_i^2 + u_j z_j^2)$$

while κ_1 is calculated as

$$\kappa_1^2 = \frac{4\pi e^2}{DkT} \cdot \frac{N}{1000} \cdot \frac{\frac{u_i z_i^2}{\rho_i} + \frac{u_j z_j^2}{\rho_j}}{\frac{1}{\rho_i} + \frac{1}{\rho_j}}$$

For a uniunivalent electrolyte, therefore, since

$$z_i = z_j = 1$$

and

$$\kappa = \kappa_1$$

we have :

$$\Delta X_i = -\frac{1}{6} \frac{e^2}{D} \cdot \frac{\kappa}{kT} \cdot (2 - \sqrt{2})X \quad . \quad . \quad (26)$$

which differs from Debye and Hückel's expression (18) only by a factor $(2 - \sqrt{2})$.

Onsager calculated the electrophoretic effect ¹ in a rather different manner from that outlined above, and he found, to a first approximation,

$$\rho_i = \frac{6\pi\eta_0}{\kappa} \quad . \quad . \quad . \quad (27)$$

The overall velocity of the ion is given in his theory by :

$$u_i = \frac{\sum_j K}{\sum_j \rho} \quad . \quad . \quad . \quad (28)$$

where $\sum_j K$ is the sum of all the forces, whilst $\sum_j \rho$ is the sum of all the frictional coefficients. The mobility v_i is defined as

¹ Onsager, *Physikal. Z.*, **29** (1928), 277.

the velocity under a total field strength $X = 1$. From (26), therefore, for a diionic electrolyte :

$$\Sigma K = ez_i \frac{\Sigma X}{300} = ez_i \frac{X + \Delta X_i}{300} =$$

$$ez_i \frac{X}{300} \left[1 - \frac{e^2 z_i z_j}{3DkT} \cdot \frac{\kappa_1^2}{\kappa + \kappa_1} \right] \quad . \quad . \quad (29)$$

Thus from (28)

$$v_i = \frac{u_i}{X} = \frac{\Sigma K}{\Sigma \rho} \cdot \frac{1}{X} = \frac{ez_i}{\Sigma \rho} \cdot \frac{1}{300} \left[1 - \frac{e^2 z_i z_j}{3DkT} \cdot \frac{\kappa_1^2}{\kappa + \kappa_1} \right] \quad . \quad (30)$$

We may write for $\Sigma \rho$,

$$\Sigma \rho = \rho_i + \frac{6\pi\eta_0}{\kappa} \quad . \quad . \quad . \quad (31)$$

so that, from (30) to a first approximation, the mobility of an ion of type i is

$$v_i = \frac{1}{300} \left[\frac{ez_i}{\rho_i} - \frac{e^2 z_i z_j}{3DkT} \cdot \frac{\kappa_1^2}{\kappa + \kappa_1} \cdot \frac{ez_i}{\rho_i} - \frac{\kappa}{6\pi\eta_0} ez_i \right] \quad . \quad (32)$$

or converting to practical units,

$$v_i \frac{ez_i}{3 \times 10^9} =$$

$$\frac{1}{9 \times 10^{11}} \left[\frac{(ez_i)^2}{\rho_i} - \frac{e^2 z_i z_j}{3DkT} \cdot \frac{\kappa_1^2}{\kappa + \kappa_1} \cdot \frac{(ez_i)^2}{\rho_i} - \frac{\kappa}{6\pi\eta_0} (ez_i)^2 \right] \quad (33)$$

Since also

$$\frac{ez_i}{300 \rho_i} z_i \left(\frac{eN}{3 \times 10^9} \right) = \frac{ez_i}{300 \rho_i} z_i F = (\lambda_\infty)_i \quad . \quad (34)$$

where F is now expressed in coulombs, we therefore have

$$(\lambda_c)_i = (\lambda_\infty)_i - \frac{e^2 z_i z_j}{3DkT} \cdot \frac{\kappa_1^2}{\kappa + \kappa_1} (\lambda_\infty)_i - \frac{\kappa}{6\pi\eta_0} \cdot N \cdot e^2 z_i^2 \quad (35)$$

Substituting for the new physical constants in equation (35), replacing κ by its proper value and expressing c , the concentration in grams per litre, we have :

$$\frac{(\lambda_c)_i}{z_i} = \frac{(\lambda_\infty)_i}{z_i} - \left[\frac{0.986 \times 10^6}{(DT)^{\frac{3}{2}}} \cdot \omega \cdot \frac{(\lambda_\infty)_i}{z_i} + \frac{29.0 z_i}{\eta_0 (DT)^{\frac{1}{2}}} \right] \sqrt{(z_i + z_j)c} \quad (36)$$

where

$$\left. \begin{aligned} \omega &= \frac{2q}{1 + Nq} \cdot z_i z_j \\ q &= \frac{\kappa_1^2}{\kappa^2} = \frac{z_i z_j}{(z_i + z_j)} \frac{[z_j(\lambda_\infty)_i + z_i(\lambda_\infty)_j]}{[z_j^2(\lambda_\infty)_i + z_i^2(\lambda_\infty)_j]} \end{aligned} \right\} \quad (37)$$

The constants z_i and z_j are of course the valencies of the ions, whilst $(\lambda_\infty)_i$ and $(\lambda_\infty)_j$ are their limiting conductivities. For a symmetrically valent electrolyte $z_i = z_j = 1$, so that in (37) $q = \frac{1}{2}$ and $\omega = (2 - \sqrt{2})z^2$. Equation (36) therefore becomes

$$(\lambda_c)_i = (\lambda_\infty)_i - \left[\frac{5.78 \times 10^5}{(DT)^{\frac{3}{2}}} z^2 (\lambda_\infty)_i + \frac{29.0 z^2}{\eta_0 (DT)^{\frac{1}{2}}} \right] \sqrt{2zc} \quad (38)$$

or for the whole salt,

$$A = A_\infty - \left[\frac{5.78 \times 10^5}{(DT)^{\frac{3}{2}}} \cdot A_\infty z^2 + \frac{58.0 z^2}{\eta_0 (DT)^{\frac{1}{2}}} \right] \sqrt{2zc} \quad (39)$$

This equation (39) has the advantage over the Debye-Hückel equation of containing no arbitrary constants. A reference to Debye's conductivity equation (23) shows that this involves an "electrophoretic radius" r_i arising from the method used in calculating the magnitude of the electrophoretic effect.¹ This arbitrary constant can only be estimated from conductivity measurements, so that an absolute calculation of the coefficient of the square root cannot be made. The electrophoretic radius was identified by Debye and Hückel with the distance of nearest approach of the ions in solution, but measurements of the refractivities of solutions show that the parameter r_i can hardly have this physical significance.²

For aqueous solutions of univalent electrolytes Onsager's equation (39) becomes :

$$A = A_\infty - (\alpha A_\infty + \beta) \sqrt{c} \quad (40)$$

¹ Onsager, *Physikal. Z.*, **28** (1927), 277.

² K. Fajans, *Trans. Faraday Soc.*, **23** (1927), 357.

where at 25° C. $\alpha = 0.2274$ and $\beta = 59.79$.¹ This equation has the same limited range of application—viz., only to those solutions in the region of infinite dilution—as Debye and Hückel's equations for the thermodynamic properties of strong electrolyte solutions (see Chapter VII). Since the theory is very limited, measurements designed to confirm it experimentally have to be made very accurately, and every care has to be taken to eliminate disturbing influences. Apart from their value in giving an experimental confirmation of the fundamental validity of the interionic theory, measurements of the conductivities of solutions (and related measurements of the transport numbers of ions) are valuable for investigating the condition of the dissolved solute in a solution. The thermodynamic properties of solutions are also dependent on the condition of the dissolved solute, but almost all the measurements of these have been made on aqueous solutions for which the dielectric constant is abnormally high. The special conditions which hold in such solutions do not allow the conclusions reached in these cases to be generalised. On the other hand, measurements of the conductivities of solutions have been made over a wide range of solvents, and a theory of these cases is more likely to be of value than one designed to explain the limited data available for thermodynamic properties.²

The Specific Conductivity of Electrolytes.

The specific conductivity of a solution is defined as the reciprocal of the specific resistance—i.e., as the reciprocal of the resistance between two faces of a unit cube when the potential between them is 1 volt.

Now, in a solution the solute only is regarded as responsible for the passage of the current (the solvent correction being important only in the most dilute solutions). It would therefore be more logical to refer the conductivity to a fixed quantity of solute in the solution instead of to a fixed quantity of solvent. For this purpose we use the equivalent

¹ These are the best values using the most accurate values for the constants involved.

² R. Fuoss, *Chem. Rev.*, 17 (1935), 27.

conductivity κ ,—i.e., the conductivity of 1 gram-equivalent of solute in a solution contained between electrodes across which there is unit potential difference and which are situated 1 cm. apart. The total conductivity between the electrodes then represents the equivalent conductivity and

$$A = \frac{\kappa}{c'} = \frac{1000\kappa}{c} = 1000\kappa V \quad . \quad . \quad (41)$$

where c is expressed in gram-equivalents per litre, c' in gram-equivalents per c.c., and V is the dilution in litres. This function A for the conductivity is independent of the current flowing through the solution, and it may therefore be used as a standard of comparison between different electrolytes. The specific conductivity falls as the dilution rises, since there are fewer molecules between the electrodes to carry the current. On the other hand, the equivalent conductivity, which measures the conductivity of a fixed quantity of the electrolyte, increases with the dilution, due to the greater number of particles present at the higher dilutions. This increase follows partly, of course, from the increased dissociation of the electrolyte at the higher dilutions (Arrhenius), and partly from the greater mobilities of the ions at the higher dilutions.

Direct-current Methods for Determining Conductivity.

Apart from Cavendish's measurements, the first determinations of conductivity employed the same direct-current methods which would now be used for the determination of any metal resistance or of a very high liquid resistance like pure water. The current was passed through a long, rectangular trough containing the liquid, and the deflection of a galvanometer in the circuit was noted; by moving the electrodes closer together through a known distance, the galvanometer deflection could then be returned to its former value by the variation of a resistance in series with the solution, the battery, and the galvanometer. The difference between the initial and final readings of the change in the wire resistance would then be the same as that of a column of the solution equal in length to the distance through which

the electrodes had been moved. The direct-current method, in this simple form, is open, however, to serious criticism when it is applied generally. Firstly, there is no means of preventing the changes in concentration which take place in the solution near each electrode due to the Hittorf transport effect of the outgoing ions. Secondly, the polarisation of the electrodes due to the discharge of atomic oxygen and hydrogen at the anode and cathode, respectively, in aqueous solutions of electrolytes, is a cumulative process during the passage of a direct current, and this causes an opposing E.M.F. to be set up in the cell. Only therefore in special cases is it possible to use a direct current method for measuring conductivities without introducing serious errors. We may quote the work of Brönsted and Nielsen¹ as an example of such a special case. These workers have employed the principle with some success for measuring the conductivities of acid and alkaline solutions. In their arrangement, polarisation is reduced to a minimum by using lightly platinised platinum electrodes. Moreover heating effects, due to the passage of the current, need never be very great, since the current is only passed for a very short time when testing the bridge setting. An attainable accuracy of 1 part in 10,000 is claimed and, where it is possible to use it, the arrangement is much simpler than an alternating current bridge designed to give the same accuracy.

The Alternating-current Wheatstone Bridge.

Almost all the methods now used depend, however, on the Wheatstone bridge principle using an alternating current to activate the resistance bridge. Kohlrausch, whose work on these measurements is classical, used alternating currents of audible frequencies which were supplied by a small induction coil, so that the null point of the bridge could be detected with a Weber dynamometer or by observing the position for minimum sound in a telephone.²

¹ J. N. Brönsted and R. F. Nielsen, *Trans. Faraday Soc.*, **31** (1935), 478.

² E. Kohlrausch and L. Holborn, "Das Leitvermögen der Elektrolyte," Leipzig (1916), pp. 34 *et seq.*

In this arrangement any film of gas formed during the passage of the alternating current in one direction is driven off when the current reverses. Similarly, changes in the concentration of the electrolyte in the region of the electrodes are counteracted by this device. Kohlrausch further reduced the tendency to accumulate relatively thick layers of gas by using heavily platinised electrodes which had a large superficial area, and which therefore reduced the current density. The accuracy with which the variable resistance in the bridge could be measured was increased by extending the virtual length of this at either end by attaching coils of known resistance to it. Measurements were made only near the centre of the whole wire, for at either end of the resistance the errors introduced in reading the position of the moving contact would be greatly magnified. The balance point was obtained on either side of the mid-point of the wire by introducing a reversing key into the circuit, and resistance changes due to the thermoelectric forces and local temperature changes were thus eliminated. Kohlrausch recommended that the wire of the resistances should be constantan with a composition 40% of nickel and 60% of copper, or that some other wire be used which, like constantan, is not oxidisable, and therefore preserves a clean surface in contact with air and which also has a low temperature coefficient of resistance.¹

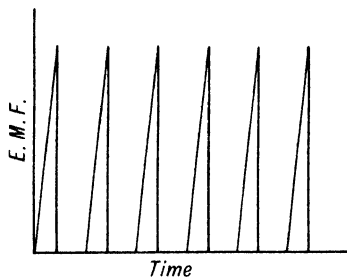


FIG. 18.—E.M.F. VARIATION FROM AN INDUCTION COIL.

The use of an induction coil as a source of alternating current is open to several objections. The nature of the E.M.F. surges from an induction coil may be studied by means of the cathode-ray oscillograph. The plot of E.M.F. against time in Fig. 18 shows that the discharge consists of a number of pulsating potential bursts. It is evident,

The use of an induction coil as a source of alternating current is open to several objections. The nature of the E.M.F. surges from an induction coil may be studied by means of the cathode-ray oscillograph. The plot of E.M.F. against time in Fig. 18 shows that the discharge consists of a number of pulsating potential bursts. It is evident,

¹ E. Kohlrausch and L. Holborn, "Leitvermögen der Electrolyte," Leipzig, 1916.

therefore, from the exact nature of the discharges that unsymmetrical polarisation must take place in the cell when an induction coil is used to actuate the bridge.¹ Moreover, an induction coil never gives complete silence in the telephone at the balance point, due to the presence of harmonics in the complex oscillations which it sets up. A valve oscillator has been found to give a fairly accurate sinoidal current, and by using the circuit shown in Fig. 19 an extremely wide range of frequencies may be obtained by varying the capacities C and C' .² The oscillator gives a

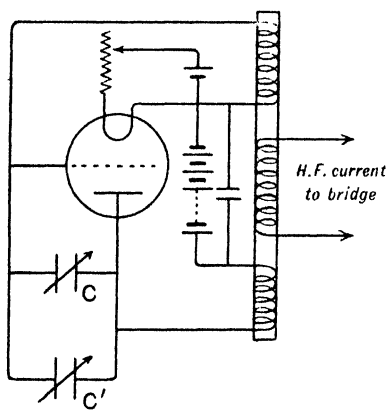


FIG. 19.—VALVE OSCILLATOR
(Hall and Adams).

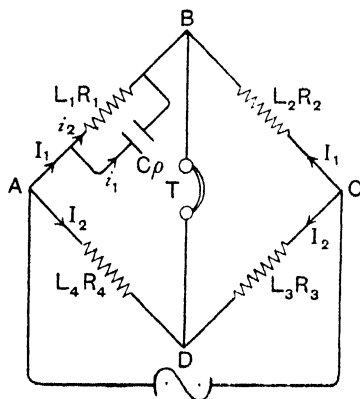


FIG. 20.—IDEALISED WHEATSTONE
NETWORK IN CONDUCTIVITY
MEASUREMENTS.

first harmonic as well as a fundamental oscillation at low frequencies, but this ceases to be important above about a thousand cycles per second. The telephone used to detect the null point in the bridge circuit may then be tuned to the frequency of the H.-F. generator.

Unfortunately the use of alternating currents in a Wheatstone network gives rise to many secondary effects, for there is self-induction in such a circuit and the conductivity cell with its parallel plate electrodes behaves

¹ W. A. Taylor and S. F. Acree, *J. Amer. Chem. Soc.*, **38** (1916), 3396.

² R. E. Hall and L. Adams, *ibid.*, **41** (1919), 1515. Compare Grinnell Jones and Josephs, *ibid.*, **50** (1928), 1053.

as a resistance in parallel with a condenser of definite capacity.¹ Consequently, the instantaneous value of the current in every arm of the bridge containing inductively wound resistances will not be the same as when induced currents are eliminated. The exact condition at the balance point may be worked out if it is remembered that the cell behaves as a resistance in parallel with a condenser. The idealised Wheatstone network in the arrangement for measuring conductivity will therefore appear as shown in Fig. 20, where L denotes inductance; R resistance; I_1 the current in the arms AB, BC ; I_2 that in the arms CD, DA ; and C and ρ are respectively the capacity and internal resistance of the condenser in the arm AB . In the arm AB the current I_1 divides into i_1 through the condenser and i_2 through the resistance. If q is the charge on the condenser plates

$$i_1 = \frac{\partial q}{\partial t} + \frac{q}{\rho c} \quad . \quad . \quad . \quad (42)$$

since $q = vc$ and the current is related to the potential by Ohm's law. For the general case of an alternating potential difference of frequency p the E.M.F. at time t is given by

$$\left. \begin{aligned} E &= E_0 e^{jpt} \\ \text{i.e.,} \quad \frac{\partial E}{\partial t} &= jp E_0 e^{jpt} \end{aligned} \right\} \quad . \quad . \quad . \quad (43)$$

where $j = \sqrt{-1}$. The operator $\frac{\partial}{\partial t}$ may therefore be replaced by jp . Thus from (42)

$$i_1 = \left(jp + \frac{1}{\rho c} \right) q$$

Now, the potential difference E_1 between A and B will be given by

$$E_1 = \frac{q}{c} + i_1 \rho = \left(\frac{i}{jpc + \frac{1}{\rho}} \right) + i_1 \rho \quad . \quad (44)$$

¹ E. W. Washburn, *J. Amer. Chem. Soc.*, **38** (1916), 2431. See also Wien, *Ann. Physik*, **58** (1906), 67, who supposes the cell to behave as a resistance in parallel with a condenser and in series with a capacity. Due to the small extent of polarisation which has the effect of the capacity, however, this supposition is, for practical purposes, the same as Washburn's.

Also, for the resistance and inductance

$$E_1 = R_1 i_2 + L_1 \frac{\partial i_2}{\partial t} = R_1 i_2 + j L_1 p i_2 \quad (45)$$

The total current I_1 is related to i_1 and i_2 by

$$I_1 = i_1 + i_2 \quad (46)$$

Thus, eliminating i_1 and i_2 from (44), (45), and (46),

$$I_1 = \frac{E_1}{\left(\frac{1}{jpc + \frac{1}{\rho}}\right) + \rho} + \frac{E_1}{R_1 + jL_1 p} \quad (47)$$

Simplifying

$$I_1 = \frac{E_1(jpcR_1 - p^2L_1C + j\frac{p^2}{\rho} + \frac{R_1}{\rho} + 2 + jpc\rho)}{(2 + jpc\rho)(R_1 + jpL_1)} \quad (48)$$

$$\text{or } E_1 = \frac{I_1(2 + jpc\rho)(R_1 + jpL_1)}{\left(2 + \frac{R_1}{\rho} - p^2L_1C\right) + j\left(pcR_1 + \frac{pL_1}{\rho} + pc\rho\right)} \quad (49)$$

In the other arms the potential drops are given simply by

$$\left. \begin{aligned} E_2 &= I_1(R_2 + jpL_2) \\ E_3 &= I_2(R_3 + jpL_3) \\ E_4 &= I_2(R_4 + jpL_4) \end{aligned} \right\} \quad (50)$$

and

At the balance point there is no current through the telephones, and the potentials at B and D are therefore equal. It follows from equations (49) and (50) that

$$\frac{R_3 + jpL_3}{R_4 + jpL_4} = \frac{2(jpc\rho + 2)(R_1 + jpL_1)}{\left(2 + \frac{R_1}{\rho} - p^2L_1C\right) + j\left(pcR_1 + \frac{pL_1}{\rho} + pc\rho\right)} \quad (51)$$

By cross-multiplying in equation (51) and equating the real parts we find :

$$R_2R_4 - p^2L_2L_4 = \frac{\rho(2R_4 - p^2C\rho L_4)(2R_1\rho + R_1^2 - p^2\rho R_1L_1C + p^2\rho CR_1L_1 + p^2L_1^2 + p^2L_1C\rho^2)}{(2\rho + R_1 - p^2L_1C\rho)^2 + p^2(\rho cR_1 + L_1 + \rho^2c)^2} \quad (52)$$

The condition

$$\frac{R_1}{R_2} = \frac{R_3}{R_4}$$

therefore does not hold at the balance point when an alternating-current bridge is used, and even if no capacity is present—*i.e.*, if $\rho = 0$ in (52)—equations of the type

$$\frac{R_1 L_2}{R_2 L_1} = \frac{R_3 L_4}{R_4 L_3}$$

are obtained as the condition for balance. The balance point cannot therefore be determined solely by an adjustment of resistances. This is, indeed, apparent in any simple network designed to measure conductivity by the fact that it is impossible to reach a point on the ratio resistances where there is no sound in the telephone. Moreover the resistance to be measured depends on the frequency, although this dependence decreases as the surface area of the electrode is increased (for example, by platinisation).¹ Such an increase in electrode surface cannot, however, be continued indefinitely, for if secondary reactions occur during electrolysis, anomalous effects are introduced by the absorption of hydrogen and oxygen in the spongy platinum electrodes.

If secondary reactions do occur during electrolysis, the bridge circuit has to be completely modified by including inductances and capacities which may be varied until they balance out the cell effects in the bridge. Capacity errors in the bridge itself are avoided by earthing the bridge and introducing inductances on both sides, one variable on the same side as the cell, one fixed on the opposite side. By balancing the bridge with the cell in and out of circuit, the difference in the variable resistance in the two cases gives the apparent resistance of the cell and leads R_p , and the difference in the inductance L_p , the resistance corresponding with the cell capacity.²

All the errors in the alternating-current Wheatstone bridge have not, however, been eliminated by simply intro-

¹ H. Hartley and W. H. Barrett, *J.C.S.* (1913), 786.

² W. A. Taylor and S. F. Acree, *J. Amer. Chem. Soc.*, **38** (1916), 2416.

ducing variable inductances and capacities on both sides of the bridge. Capacity effects between the observer and the telephone may cause a charging current which would upset the balance of the bridge and prevent a sharp minimum. It is therefore necessary to eliminate this effect by arranging for both the observer and the telephone to be at the ground potential when the actual observation of the balance point is made. This may be successfully achieved by connecting in parallel with the bridge a variable resistance and condenser, the middle point of the resistance and one side of the condenser being earthed ¹ (a modification of the Wagner earthing device ²). If, then, the telephones are arranged so that one side remains fixed to the bridge

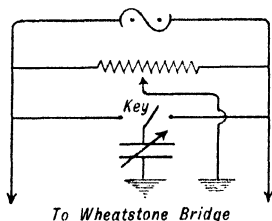


FIG. 21.—WAGNER EARTH-
ING DEVICE.

while the other side is connected alternately to the other side of the bridge or to earth, the bridge may first be balanced with the telephone across the bridge and then, after earthing one side of the telephone (and therefore the bridge), adjusting the variable resistance and capacity until there is silence in the telephone. The bridge is now at ground potential, and a final adjustment of this with the telephone in circuit gives the true reading at the balance point with both the telephone and the observer at the common ground potential.

In order to obtain delicate balances it is necessary to screen the bridge adequately from external electrical disturbances, besides eliminating current losses to objects near by. The presence of electrical apparatus in the vicinity of the bridge, and even the shifting capacities introduced by the observer himself, all have an important effect when very accurate results are required. Shedlovsky has carried out a very careful investigation of the nature of capacity effects with a view to discovering how they may best be

¹ Grinnell Jones and Josephs, *J. Amer. Chem. Soc.*, **50** (1928), 1049.

² Wagner, *Electrotechnische Zeitschrift*, **32** (1911), 2011.

compensated.¹ He finds that these disturbances can only be eliminated by screening the whole bridge together with the leads to and from the oscillator and the cell. The shielding itself consists of thin copper sheeting built up and connected symmetrically on both sides of the bridge. Reaction due to polarisation in the cell may be balanced out by a variable air condenser connected across the measuring resistance and the cell. The detector consists simply of a carefully constructed transformer-coupled amplifier connected to sensitive telephones. In this form, using a valve oscillator, the apparatus has the advantage that measurements may be made at several frequencies. As most electrical errors change with the frequency of the alternating current, measurements taken over a range of frequencies will show whether electrical errors arising from the bridge design are being compensated.

The Conductivity Cell.

The construction of the conductivity cell also has an important effect on the accuracy of conductivity measurements. Furthermore, the greatest care has to be exercised in all measurements, to ensure very careful temperature control and the high purity of the substances used in the preparation of the solutions. Dissolved ammonia and carbon dioxide, and even soluble alkali present in ordinary glass containing vessels, seriously affect the measurements in dilute solutions. Conductivity cells for accurate work are therefore usually constructed from fused quartz or some resistant glass. The shape of the vessel should also be chosen so that anomalous capacity effects are minimised and so that no lines of current-flow in the electrolyte escape to the surface.² Most dilution experiments have been carried out with cells of the Ostwald type³ (Fig. 22), which have a small hole through the ebonite cover into which a pipette may be inserted for effecting dilution. The electrodes

¹ T. Shedlovsky, *J. Amer. Chem. Soc.*, **52** (1930), 1793.

² E. W. Washburn, *ibid.*, **38** (1916), 2431.

Shedlovsky, *ibid.*, **52** (1930), 1816.

Grinnell Jones and Bollinger, *ibid.*, **53** (1931), 411.

W. Ostwald, *Z. physikal. Chem.*, **2** (1888), 561.

are circular platinum discs each attached to a platinum wire fused into glass tubes which pass out through the cover.

For non-aqueous solutions, however, a different arrangement has been used. Non-aqueous solvents are frequently more volatile than water, and their properties are almost always very sensitive to the presence of traces of moisture. For these measurements it is therefore advisable to start with a considerable quantity of solvent in a cell where it is protected from contamination with the air, and to add to this small measured quantities of the electrolyte solution from a volume pipette. The cell is constructed of some resistant glass¹ with an outside ground cap to prevent the

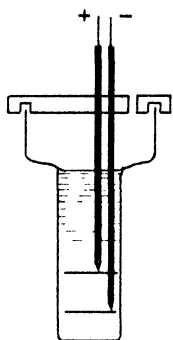


FIG. 22.—OSTWALD DILUTION CELL.

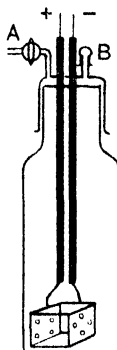


FIG. 23.—HARTLEY-BARRETT CELL FOR NON-AQUEOUS SOLUTIONS.

accumulation of dust where it might fall in on removing the cap.² The electrodes are arranged as two parallel plates pierced with holes and held together by four corner pillars of glass. When the cap of the cell is rotated, the solution inside is stirred, by the movement of the electrodes, without exposure to the atmosphere. During the addition of any solution through *B* (Fig. 23) a current of pure air, saturated with the solvent, is passed from the tap *A* through the cell, again preventing any contamination of the solution by moisture. Even when this effect has been counteracted,

¹ Recent work appears to show that, apart from quartz, Pyrex is the most resistant glass from the point of view of its effect on the conductivity of pure water and of dilute solutions (S. J. Kiehl and S. B. Ellis, *J. Amer. Chem. Soc.*, **57** (1935), 2139, 2145).

² H. Hartley and W. H. Barrett, *J.C.S.* (1913), 786.

the problem of the design of the conductivity cell has not been completely solved.

In the type of cell which has simple dipping electrodes like the Hartley-Barrett cell for non-aqueous solutions, further errors may arise from the development of parasitic currents in the system. In the simple arrangement of the dipping electrodes such as that shown in Fig. 24, the total current which is measured in the bridge is made up of two parts. One of these is the current flowing directly between

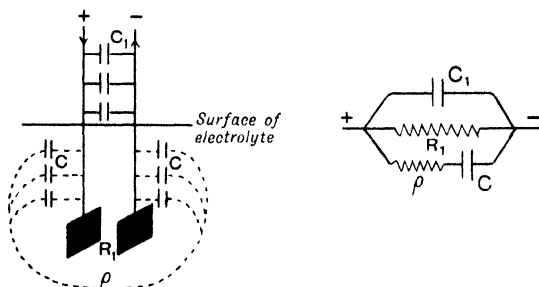


FIG. 24.—CURRENT FLOW IN AN ARRANGEMENT OF DIPPING ELECTRODES.

the electrodes through the electrolyte of resistance R_1 , together with that through the capacity C_1 between the plates. The other is a parasitic current which flows, through a capacity c and a resistance path ρ , between those portions of the leads in the solution. Remembering that in the bridge the cell is balanced by a resistance R_2 and a capacity C_2 in parallel, we have :

$$\frac{1}{R_2} + jpC_2 = \frac{1}{R_1} + jpC_1 + \frac{1}{\rho - \frac{j}{pc}} \quad (53)$$

Solving this for $\frac{1}{R_2}$

$$\frac{1}{R_2} = \frac{1}{R_1} + \frac{1}{\rho + \frac{1}{p^2c^2\rho}} \quad (54)$$

and since ρ depends on the resistance of the solution, it is

proportional to R_2 —i.e. $\rho = \alpha R_1$ —or, substituting for ρ and expanding the last term in equation (54):

$$\frac{1}{R_2} = \frac{1}{R_1} \left(1 + \frac{1}{\alpha} - \frac{1}{p^2 c^2 \alpha^2 R_1} + \dots \right) \quad (55)$$

This equation could only be used to correct the bridge reading for the errors arising in this simple cell with immersion electrodes, if the values of ρ and c were known. In general, it is necessary to avoid making this difficult correction by using electrodes of such a design that parasitic currents are reduced.¹ These effects may be minimised by taking the leads to the electrode plates out of the cell in opposite directions at right angles to the electrode plates. Moreover, the quantity of electrolyte between the plates must be made as large as possible in comparison with the length of exposed lead wires in the electrolyte. In cells for measuring the conductivity of highly resistant liquids, where the plates must be very close together, these should be brought almost flush with the glass sides of the cell.

Now, in general the lines of current flow are not the same even with the same cell when two different solutions are measured in it. If two solutions are measured, the one having a high, the other a low conductivity, complicating factors will therefore arise depending on the absolute values of the specific conductivities of the solutions and on the depths to which the cell is filled in each case, and these have an important effect on the accuracy of the measurements. The value of the cell constant (i.e., the factor by which the reciprocal of the measured resistance must be multiplied to give the specific conductivity) for a highly resistant solution, appears to be different from its value for a more highly conducting solution,² and this difference may amount in certain cases to 1 part in 300. This so-called "Parker effect" was formerly attributed to the difference of resistance between adsorbed layers of electrolyte in the immediate

¹ Shedlovsky, *J. Amer. Chem. Soc.*, **54** (1932), 1411.

² H. C. Parker, *ibid.*, **45** (1923), 1366, 2017.

Randall and Scott, *ibid.*, **49** (1927), 1636.

F. A. Smith, *ibid.*, **49** (1927), 2167.

vicinity of the electrode surface and the body of the solution.¹ The anomaly has, however, now been traced to the type of pipette cell used in the measurements of the conductivities. In these cells the electrodes are set horizontally one above the other and the filling tubes and contact tubes to the electrodes are all close together. Consequently the resistance of the electrolyte is being shunted by the resistance and the capacity in the filling tube through the glass walls of the cell and the thermostat oil

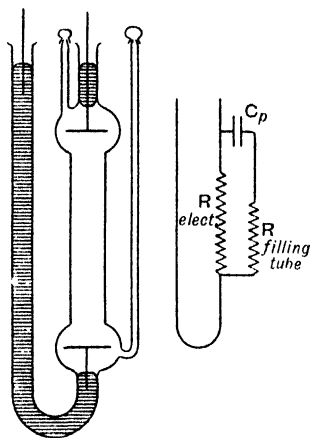


FIG. 25.—PIPETTE CELL SHOWING SHUNT EFFECT OF THE FILLING TUBE.

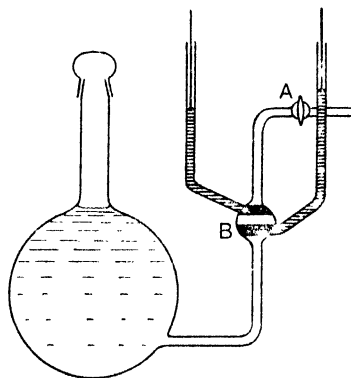


FIG. 26.—SHEDLOVSKY'S "FLASK" CELL.

between the solution in the filling tube, which have one polarity, and the mercury in the nearest contact tube which has an opposite polarity² (see Fig. 25). The difficulty is overcome by separating the filling tubes as far as possible from the contact tubes of opposite polarity (about 15 cm. is found to be sufficient). This is best accomplished by arranging the long tube containing the electrolyte between the electrodes horizontally and taking the filling tubes out to the extreme right and left. In very dilute solutions all the errors of measurement due to an ill-designed apparatus

¹ H. C. Parker, *J. Amer. Chem. Soc.*, **45** (1923), 1366, 2017.

² Grinnell Jones and Bollinger, *ibid.*, **53** (1931), 411.

become very much more important than in solutions of ordinary concentrations. The best-designed conductivity cells for measurements on these types of solution have the electrodes taken out of the flask, where the large quantity of solution is kept, into a side tube as shown ¹ (Fig. 26). The electrode leads can then be separated as far as possible from one another by the oil of the thermostat.² The only capacity effect likely to be of any consequence would be to earth from the relatively large surface of the flask, and the terminal *M* nearest to this is therefore connected to the terminal of the bridge which is kept at earth potential. The cell proper is the small bulb *B* in which the electrodes are two hollow, pierced platinum cones fused at all points of their outer surfaces to the glass. A stream of purified nitrogen passed into *A* at different pressures enables the solution to be filled into or emptied from the cell *B*. The solution can be prepared in the flask by passing a stream of nitrogen from *A* with the stopper lifted and quickly adding an increment of the solute to the solution from a weight burette.

Before the conductivities of solutions can be determined, the cell must first be calibrated by using potassium chloride solutions the conductivities of which have been accurately determined.³ As a standard substance potassium chloride has the advantages over other standards that it is easily purified, is non-hygroscopic (an important factor when the substance has to be weighed accurately), is sufficiently soluble, and is stable both in the solid form and in its solutions. If the conductivity of the potassium chloride is known, the conductivity of any other solution measured in the same cell may then be obtained as follows. If *A* be the conductivity, measured in the cell, of an *N*/100 potassium chloride solution at 18° C. (for which the specific conductivity is 0.00122052 reciprocal ohm per cm.) and *A'* be the

¹ T. Shedlovsky, *J. Amer. Chem. Soc.*, **54** (1932), 1411.

² The importance of using oil as a thermostat liquid instead of water which is a conductor has been emphasised by Grinnell Jones and Josephs, *ibid.*, **50** (1928), 1045.

³ Grinnell Jones and Bradshaw, *ibid.*, **55** (1933), 1780.

Grinnell Jones and Prendergast, *ibid.*, **59** (1937), 731.

conductivity for the unknown electrolyte solution of specific conductivity κ' , then

$$\frac{\kappa'}{0.00122052} = \frac{A}{A'} \quad . \quad . \quad . \quad (56)$$

$$\text{i.e.,} \quad \kappa' = \text{cell constant} \times A' = CA' \quad . \quad . \quad (57)$$

In this equation the "cell constant" C , which is dependent only on the dimensions of the cell, is given by $\frac{0.00122052}{A}$.

It is assumed that the lines of current flow are the same in each case—i.e., that the cell conforms to the principles of design laid down above.

The Conductivities of Pure Solvents.

When due attention is given to the construction of the cell and the bridge, the accuracy which can be attained in conductivity measurements renders it necessary to know exactly the contribution of the pure solvent to the measured conductivity. This "solvent correction" becomes more and more important as the dilution increases, and since it is especially in the range of very dilute solutions that the most accurate measurements are required for verifying the interionic attraction theory, the methods for measuring and applying the correction must now be investigated in detail. It should, however, be noted that the correction for solvent effect is of much greater importance in the study of irreversible processes than in the determination of the thermodynamic properties. In the latter case, the activities of the different ions, which determine the measured effect, are practically identical, whereas their mobilities differ considerably. The replacement of one ion by another in irreversible processes in electrolytes may therefore have a considerable effect on the measured property while scarcely affecting the thermodynamic properties. For the present, only aqueous solutions will be considered. An approximate calculation of the least magnitude of the solvent correction in very dilute aqueous solutions may be made from the measurements of Kohlrausch. He found that the conductivities of solutions of strong electrolytes at dilutions of

$\text{N}/10,000$ were of the order of magnitude 10^{-5} to 10^{-6} reciprocal ohm. Now, the best measurements of the conductivity of the purest water available give a value 3.77×10^{-8} reciprocal ohm at 18°C . (Kohlrausch and Heydweiller), so that even if water of this low conductivity could be used for making up the solutions, the solvent correction would in some cases amount to nearly 5% of the total conductivity. Water of such a low conductivity can never be used for conductivity measurements of solutions, and in most cases the solvent correction would be very much greater than 5% at high dilutions. It is, however, necessary to use solvent of the highest purity possible under the experimental conditions (see below), and it must be kept free from contamination during the preparation of the solutions, so that its effect on the measured conductivity may remain constant throughout the experiment.

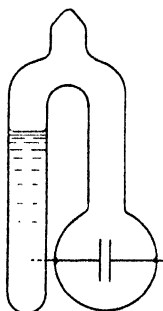


FIG. 27.—
KOHLEAUSCH-
HEYDWEILLER
CELL.

For water, the non-volatile impurities are the least important, since a single distillation in a resistant glass or metal apparatus will remove the bulk of these. Carbon dioxide and ammonia are the most difficult of the volatile impurities to remove, and since they both dissolve in water, forming highly conducting solutions, they will have a considerable influence on the conductivity of the water—i.e., on the solvent correction.¹

Kohlrausch and Heydweiller² obtained very pure water by the repeated distillation of ordinary distilled water *in vacuo* at low temperatures where only the water-soluble gases had any appreciable vapour pressure. A final distillation was then made into a Ω -shaped vessel (Fig. 27) which had been kept standing in pure water for many years in order to remove all soluble materials as completely as possible from the surface of the glass. The water in this vessel was boiled before sealing off, so that only water and

¹ J. Kendall, *J. Amer. Chem. Soc.*, **38** (1916), 2460.

² Kohlrausch and Heydweiller, *Wied. Annalen*, **53** (1894), 209; *Z. physikal. Chem.*, **14** (1894), 326.

water vapour were present. By distilling the water out from the left-hand limb into the side in which the electrodes were sealed, the conductivity could be determined at once without giving time for it to attack the glass. The value so obtained was 0.043×10^{-6} reciprocal ohms, and a correction for the irremovable impurities was made by observing the temperature coefficient of the conductivity and comparing this with the thermodynamically calculated value. The final value given for the conductivity of pure water was 0.0377×10^{-6} reciprocal ohm at 18°C. , which gives for the ionic product of water at 25°C. :

$$K_w = (\text{H}^+)(\text{OH}^-) = 1.04 \times 10^{-14} \quad (\text{see p. 13}).$$

Such a sample of water, in which the observed conductivity is due almost exclusively to the contributions made by the hydrogen and hydroxyl ions present, could not possibly be used for the measurements of the conductivities of solutions. On exposure to the atmosphere this very pure water would immediately absorb gases from the air, giving new ions which cause an immediate rise in conductivity. Kohlrausch and Heydweiller gave the following figures for the conductivity in reciprocal ohms when the pure water was exposed to air:

Original specific conductivity *in vacuo*

$$= 0.05 - 0.11 \times 10^{-6}$$

Specific conductivity after 20 minutes $= 0.4 - 0.6 \times 10^{-6}$

Specific conductivity after long standing $= 0.6 - 0.665 \times 10^{-6}$

The average of the values recorded by many workers for the conductivity of pure water is $0.55 - 0.70 \times 10^{-6}$ reciprocal ohm. For accurate work on the conductivities of dilute aqueous solutions it is therefore necessary to use a specimen of water, not of the highest degree of purity such as that obtained by Kohlrausch, but one which has the lowest specific conductivity under the experimental conditions.

In order to prepare conductivity water for ordinary purposes, ammonia and carbon dioxide, the two most persistent impurities, have to be removed. Phosphoric acid is found to be the most effective reagent when added

to the water to be distilled for removing the former gas.¹ The carbon dioxide may be removed almost entirely at one distillation by using a principle first adopted by Bourdillon.² The steam passes through an efficient water-spray trap into the middle of a condensing column, and is then forced upwards by a stream of purified air. The column is surrounded at its upper end by a condenser kept at about 50° C. and at its lower end by a cold-water condenser. By regulating the stream of air until about half the steam is condensed, almost all the carbon dioxide is carried off with the steam, for this gas is many times more soluble in steam than in water. The condensed water may then be run into Pyrex storage vessels sealed from atmospheric impurities by sof nolite and sulphuric acid.

The Application of the Solvent Correction.

The method of applying the correction for the conductivity of the solvent has caused some controversy. Kendall, for example, supposed that the purest water which could be used for conductivity work was in fact a solution saturated with carbon dioxide at its vapour pressure in the air, and he concluded that the specific conductivity of a solution of carbon dioxide at any given temperature would be proportional to the square root of the partial pressure of the gas in the solution.³ If such water were used, however, for accurate conductivity measurements, the conductivity of the water would change with conditions even during one determination, and the solvent correction could never be made with certainty.

The conductivity determination should ideally be made with the purest solvent obtainable under the experimental conditions. These conditions may, of course, be improved by carrying out the determinations in the absence of air, so that the solvent correction is reduced. Obviously the magnitude of the solvent correction for each impurity will

¹ S. J. Kiehl and S. B. Ellis, *J. Amer. Chem. Soc.*, **57** (1935), 2139.

² R. Bourdillon, *J.C.S.* (1913), 786.

C. Kraus and J. Dexter, *J. Amer. Chem. Soc.*, **44** (1922), 2468.
H. Wieland, *ibid.*, **40** (1918), 131.

³ J. Kendall, *ibid.*, **38** (1916), 1480, 2460.

depend, qualitatively at least, on the nature of the impurity and the chemical identity of the solute. Carbon dioxide as an impurity in water would have practically no effect on the conductivity of a solution of a strong acid, but its effect in reducing the conductivity of a strong base would be considerable. The actual quantitative effect of the impurity in the solvent may be found for weak electrolytes from the mass law and for strong electrolytes from the square-root law (at least, in aqueous and alcoholic solutions where this is obeyed accurately in very dilute solutions). If a determination of the solvent conductivity is made with each new set of determinations, taking account of the nature of the impurities, the solvent correction may then be applied with confidence. Further, as a check on the validity of the solvent correction, data obtained with different samples of the solvent at the same concentration of the solution should, after correction, give results which are in agreement with one another.¹

The Conductivities of Dilute Aqueous Solutions.

We are now in a position to discuss the results which have been obtained by adopting all these precautions in determining the conductivities of very dilute solutions. The most accurate measurements of the conductivities of dilute aqueous solutions which have been made in order to verify the interionic theory experimentally are to be found in the work of Shedlovsky.² Some of these results are exhibited in Fig. 28. Here the broken lines represent in each case the limiting Onsager slope calculated from equation (39):

$$\Lambda = \Lambda_{\infty} - \left[\frac{(0.9838) \times 10^6 \cdot \omega \cdot \Lambda_{\infty}}{(DT)^{\frac{1}{2}}} + \frac{28.957}{\eta(DT)^{\frac{1}{2}}} \right] \sqrt{2z\gamma^2}$$

and it will be seen that as the concentration decreases so that the conditions approach more closely to those for

¹ W. F. K. Wynne-Jones, *J. Physical Chem.*, **31** (1927), 1649.

² Shedlovsky, *J. Amer. Chem. Soc.*, **54** (1932), 1411.

Shedlovsky and MacInnes, *ibid.*, **54** (1932), 1429.

Shedlovsky and A. S. Brown, *ibid.*, **56** (1934), 1066.

Shedlovsky, Brown, and MacInnes, *Trans. Electrochem. Soc.*, **64** (1934), 14.

Shedlovsky, MacInnes, and Longsworth, *Chem. Rev.*, **13** (1933), 29.

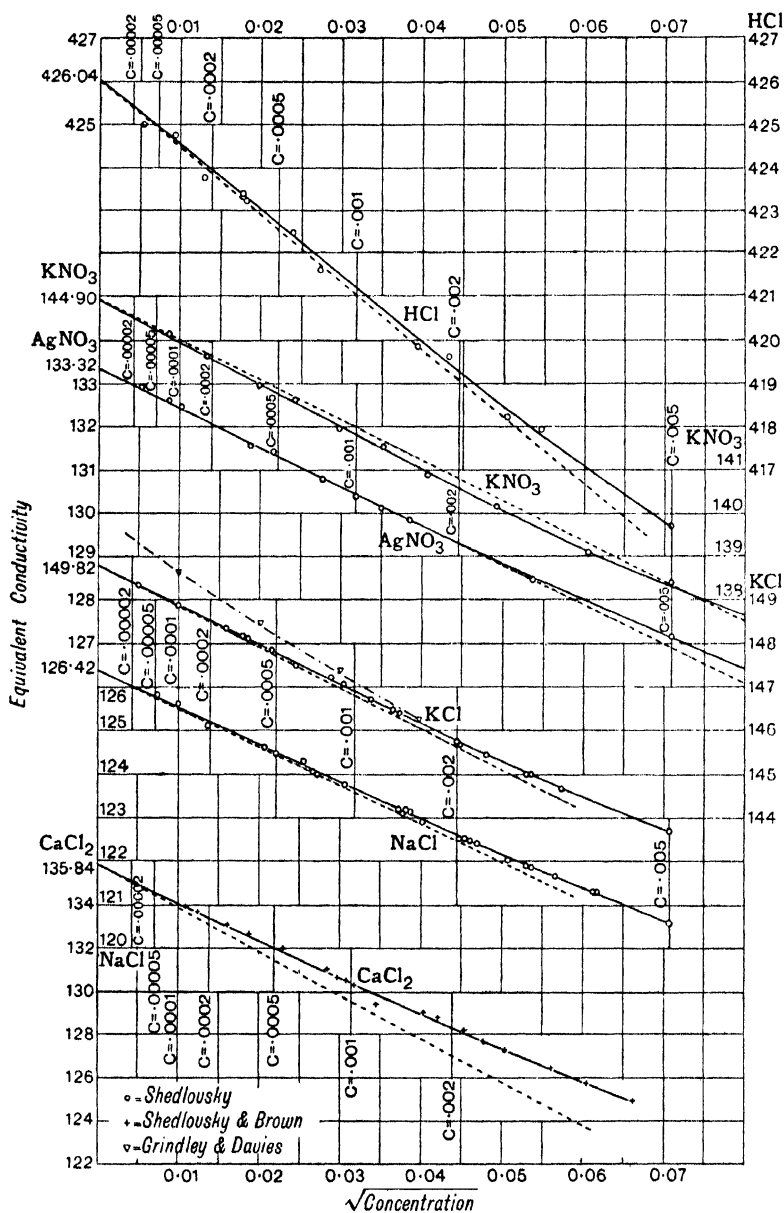


FIG. 28.—CONDUCTIVITY CURVES FOR SOME ELECTROLYTES.

which the theory applies, the experimental curve and the limiting Onsager slope correspond more nearly to one another. On this diagram the best results for potassium chloride which had been obtained before Shedlovsky made his measurements are also plotted.¹ It is at once apparent from the difference in the limiting slopes of these curves that uncorrected capacity errors and a bad design of conductivity cell have quite a large effect on the experimental results.²

The conductivities of electrolytes of valency types other than uni-univalent salts do not agree so well with the theory. In the earlier measurements large deviations from the limiting predicted slopes have, however, been traced to the presence on the experimental curves of a point of inflection very close to the axis of concentration. The limiting experimental slopes which were reported before this effect had been observed are not therefore correct.³ Accurate measurements which have been made on the conductivities of di-divalent salts like magnesium sulphate give conductivity curves which agree well with the predicted limiting slopes.⁴ The largest deviations from the theoretical equation have been observed in the case of unsymmetrically valent electrolytes where, from the difference of charges on the central ions and on the ions present in the ion atmosphere, it might be expected that complicating influences would have a most marked effect. Of the uni-univalent electrolytes, potassium and silver nitrates show the least agreement, within the limiting range, with the predicted curves, and it has been suggested that this is due to appreciable ion association even in the most dilute solutions of these salts.⁵

¹ Grindley and Davies, *Trans. Faraday Soc.*, **25** (1929), 129.

² Even with the most accurate determinations, however, the conductivities of KNO_3 and AgNO_3 and of many thallos salts are anomalous even at very low concentrations. It has been suggested (*e.g.*, R. A. Robinson and C. W. Davies, *J.C.S.* (1937), 574) that this may be due to the incomplete dissociation of these salts even at the lowest concentrations where measurements have been made.

³ R. Fuoss, *Chem. Rev.*, **17** (1935), 27.

⁴ N. K. Sementschenko, B. V. Jerofejer, and V. V. Serpinski, *Z. physikal. Chem. (A)*, **167** (1934), 197.

⁵ Robinson and Davies, *loc. cit.*

Extensions of the Theory of Conductivity.

The interionic attraction theory applied to irreversible processes in general has been extended by the application of special mathematical methods to the general case where there are any number of ionic species present.¹ The general equation obtained is very unwieldy, and has been applied to the case of conductivity, only when there are at most three ionic species present. No accurate measurements are as yet available for comparison with Onsager's generalised theory, but qualitative agreement has been found where measurements have been made, and in particular the predicted effect, that the conductivities of the two components shall not be additive, has been confirmed.²

Many attempts have been made to extend the range of applicability of the Onsager equation. Onsager has shown that the next term in his approximated equation should, if not negligible, be linear with concentration. The extended expression has been used, in order to obtain the limiting slopes and the values of conductivities at infinite dilution from the experimental results, by extrapolating observed measurements at finite but low concentrations, to infinite dilution. Such an extension is, however, valid only up to several thousandths normal, and is therefore only of value in those few cases where very accurate experimental data are available over this range. Lattey proposed the empirical equation

$$\Lambda_{\infty} - \Lambda = \frac{A'}{V + N} \quad . \quad . \quad . \quad (58)$$

in which A' and N were adjustable constants³ specific for the salt and for the temperature. Putting $V = 1/c$, (58) may be written as

$$\Lambda = \Lambda_0 - \frac{A\sqrt{c}}{1 + N\sqrt{c}} \quad . \quad . \quad . \quad (58a)$$

¹ Onsager and Fuoss, *J. Physical Chem.*, **36** (1932), 2689.

² Bray and Hunt (mixtures of HCl and NaCl), *J. Amer. Chem. Soc.*, **33** (1911), 781.

Gortner and Kay-Smith, *J. Physical Chem.*, **37** (1933), 79.

³ R. T. Lattey, *Phil. Mag.*, **4** (vii) (1927), 831.

This equation, however, gave values for the limiting conductivity which were too high, if (as Shedlovsky has shown) the Onsager equation is valid for very dilute solutions, and the value of the constant A is not equal to the correct limiting slope ($\alpha\Lambda_\infty + \beta$). Shedlovsky¹ showed that if the limiting Onsager equation (40) be written in the form

$$\Lambda_\infty = \frac{A + \beta\sqrt{c}}{1 - \alpha\sqrt{c}} \quad . \quad . \quad . \quad (59)$$

the addition of an empirical term, linear in concentration, to this expression for Λ_∞ , gave an equation

$$\left. \begin{aligned} \Lambda_\infty &= \frac{A + \beta\sqrt{c}}{1 - \alpha\sqrt{c}} + Bc \\ \text{or} \quad \Lambda &= \Lambda_\infty - (\alpha\Lambda_\infty + \beta)\sqrt{c} + Bc(1 - \alpha\sqrt{c}) \end{aligned} \right\} \quad (60)$$

which conformed to Onsager's prediction of the nature of the next term in his derivation. The equation is obeyed accurately by symmetrically valent electrolytes in aqueous solutions up to concentrations of 0.1N. Moreover it has an advantage in that, being only semi-empirical, it reduces to the Onsager limiting law, and therefore agrees with the experimental data within the limiting range as well as at higher concentrations.² For unsymmetrically valent electrolytes, however, equation (60) does not represent adequately the variations of Λ . Jones and his collaborators,³ from their measurements on the conductivities of 1:3 and 1:4 valent electrolytes find that Λ may be represented as a function of c by introducing two new parameters into equation (60) so that

$$\Lambda_\infty = \frac{A + \beta\sqrt{c}}{1 - \alpha\sqrt{c}} + Bc + Dc \ln c + Ec^2 \quad . \quad (61)$$

All the experimental points available must be used in calculating the values of the parameters, but once the curve is constructed, fairly accurate values for Λ_∞ and $\left(\frac{d\Lambda}{d\sqrt{c}}\right)_{c \rightarrow 0}$ may be found by extrapolation.

¹ Shedlovsky, *J. Amer. Chem. Soc.*, **54** (1932), 1405.

² Shedlovsky, Brown, and MacInnes, *Trans. Electrochem. Soc.*, **66** (1932), 14.

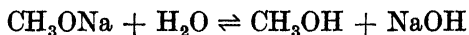
³ Jones and Bickford, *J. Amer. Chem. Soc.*, **56** (1934), 602.

Jones and Jelen, *ibid.*, **58** (1936), 2561.

The Conductivities of Non-aqueous Solutions.

Measurements of the conductivities of electrolytes in non-aqueous solutions have unfortunately not been made with the same accuracy as for aqueous solutions. Experimental data on these solutions are of great value, since, in solvents of low dielectric constants, the interionic forces are greatly increased and all the effects observed in aqueous solutions over a very wide concentration range, will be apparent within a much more limited range. The same precautions must be taken as in measurements on aqueous solutions over the preparation of the solvent in as high a state of purity as possible, consistent with easy reproducibility. An extended series of observations on methyl and ethyl alcoholic solutions has been made,¹ and some of the precautions taken in the preparation of "conductivity" methyl alcohol² may be described as illustrating the main types of difficulties which have been encountered in the preparation of such solvents.

The chief impurities in commercial methyl alcohol, apart from volatile impurities such as carbon dioxide and ammonia, are acetone, formaldehyde, and water. Of these, water is the most difficult to remove. At the same time it has a greater influence on the conductivity of pure methyl alcohol than any other impurity. Distillation over quicklime wastes a considerable quantity of the alcohol by retaining it in the lime, and the majority of the water present is best removed by fractionation under a still head. Sodium methoxide cannot be used to remove the last traces of water as the reaction



is reversible, but this difficulty is not important with aluminium methoxide. With this reagent the position of the equilibrium is far over on the side of the insoluble aluminium

¹ Frazer and Hartley, *Proc. Roy. Soc., A*, **109** (1925), 351.

D. M. Murray-Rust and Hartley, *ibid.*, **A**, **126** (1920-1930), 54.

Hartley and Bell, *Trans. Faraday Soc.*, **23** (1927), 396.

Hartley and Copley, *J.C.S.* (1930), 2488.

Hartley, Murray-Rust, and Copley, *ibid.* (1930), 2491.

² Weissberger and Proskauer, "Organic Solvents," Oxford (1935), 114, give full references to the literature.

hydroxide. The carbon dioxide and ammonia may best be removed by refluxing with dehydrated copper sulphate in a stream of pure dry air followed by distillation, as in the case of water, into a block tin condenser.¹ The detection of traces of water in the alcohol is a matter of some difficulty, for dehydrated copper sulphate forms a blue double compound with methyl alcohol which closely resembles hydrated copper sulphate. The most sensitive method depends on Goldschmidt's observations² that the conductivity of pure methyl alcoholic hydrogen chloride is influenced by the presence of traces of water to an extent quite out of proportion to its influence on any of the other physical properties of the solution. If therefore a sample of the purified methyl alcohol be used for the preparation of a solution of hydrogen chloride of known strength and the conductivity of this determined, a comparison of the result with the standard value found with methyl alcohol which is known to be pure, will show whether traces of water are present. In the presence of even very small quantities of water, the conductivity may be 25% below the value for pure solutions of the same strength.

A wide series of experiments on the alcoholic solutions of strong electrolytes were made with an assembly of the Kohlrausch-Wheatstone bridge type with a variable condenser connected in parallel with the standard arm of the network to balance capacity differences between the cell and the resistance coils. The influence of parasitic currents is very much smaller in affecting the measurements of most non-aqueous solutions than when water is the solvent, for, due to the much smaller dielectric constants, these currents are negligible. Results obtained after allowing for the solvent correction show that the salts which are strong electrolytes in aqueous solutions conform to the square-root law when dissolved at high dilutions in non-aqueous solvents. Indeed, in general, electrolytes fall into the same two sharply divided groups as in aqueous

¹ Hartley and Raikes, *J.C.S.*, 127 (1925), 525.

² Goldschmidt and Thuessen, *Z. physikal. Chem.*, 81 (1912), 30.
Goldschmidt, *ibid.*, 108 (1924), 121.

solutions—viz., those to which the square-root law applies and those the behaviour of which is adequately explained by the Ostwald dilution law.¹ This is particularly well illustrated by plotting, for the various electrolytes, the values of the Arrhenius degree of dissociation (equation 4) against the square root of the concentration, when the division between the two groups becomes clear (Fig. 29).

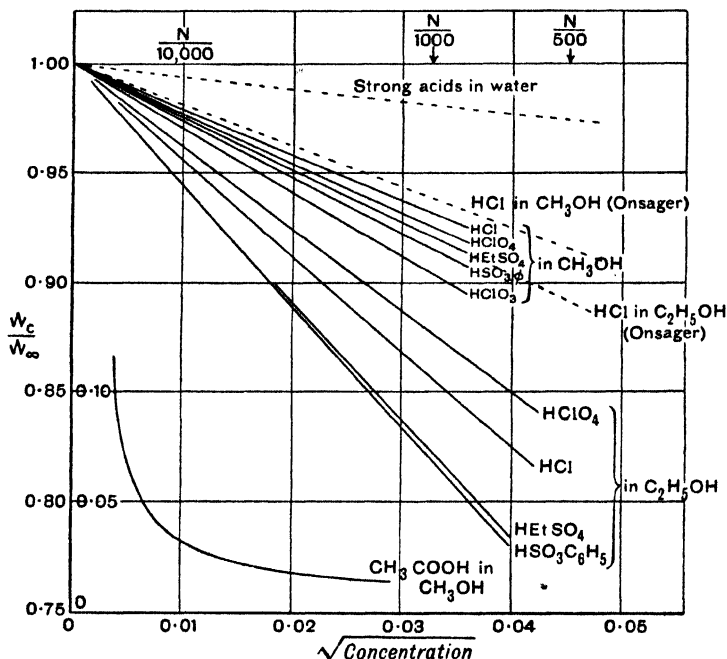


FIG. 29.—CONDUCTIVITIES OF SOME ELECTROLYTES IN ALCOHOLS.

The experimental results for solutions of strong electrolytes in hydroxylic solvents other than water do not, however, verify the Onsager equation, and the marked deviations from the limiting law are attributed by Hartley to ionic association.² The experimental curves do not even extrapolate to the predicted limiting equivalent conductivities, but this is probably due to the lack of accurate measurements in the

¹ Fraser and Hartley, *loc. cit.*

² Murray-Rust and Hartley, *loc. cit.*

region of very dilute solutions. Certainly, in solvents of dielectric constant lower than that of water, the range over which the Onsager equation can be applied with accuracy is much reduced. The general requirement of the interionic attraction theory is that the rate of change of the equivalent conductivity with concentration shall increase as the dielectric constant of the medium diminishes, in consequence of the increased electrical attraction between the ions. Measurements in methyl and ethyl alcohols confirm this only qualitatively, for the deviations from the limiting Onsager slopes are considerable even for hydrogen chloride in methyl alcohol, and they are greater still for solutions of this electrolyte in ethyl alcohol.¹

Similar but even greater deviations have been observed in nitromethane and nitrobenzene.² In these solvents practically the only salts which behave as strong electrolytes (*i.e.*, as if they were completely dissociated) are the tetra-alkylammonium picrates and chlorides. Only to these cases therefore can the Onsager equation be applied.

The hypothesis that ionic association enters at high dilutions has been used to account for the observed deviations from Onsager's law in non-aqueous solutions. It can be put to an unequivocal test by observations of the Wien effect.³ Wien first observed that there is an increase in the conductivity of an electrolyte solution under high fields⁴ (see p. 106), and it has been found that weak electrolytes

¹ Goldschmidt and Schjerve, *Z. physikal. Chem.*, **89** (1915), 129.

Murray-Rust and Hartley, *loc. cit.*

A review of measurements in many solvents is given by Hartley, Macfarlane, Gatty, and Murray-Rust, *Ann. Rep. Chem. Soc.*, **27** (1930), 339.

² Murray-Rust, Hadow, and Hartley, *J.C.S.* (1931), 215.

W. F. K. Wynne-Jones, *ibid.* (1931), 795.

Walden, *Z. physikal. Chem. (A)*, **163** (1933), 263, 321.

In many other solvents in which the conductivities of the tetra-alkylammonium salts have been measured, the square-root law is obeyed over the range of very high dilutions, but the limiting slopes do not always conform to the theoretically predicted slopes.

P. Walden, H. Ulich, and F. Lann, *Z. physikal. Chem.*, **114** (1924), 275.

P. Walden, H. Ulich, and E. Busch, *ibid.*, **123** (1926), 629.

³ G. Bauer, *Ann. Physik.*, **6** (v) (1930), 253.

⁴ M. Wien, *ibid.*, **83** (iv) (1927), 327; **85** (iv) (1928), 795.

show a much-enhanced dissociation field effect superposed upon the normal Wien effect which is observed for strong electrolytes. This is attributed to a large increase in the ionic dissociation under the high field. Obviously therefore an investigation of the Wien effect for non-aqueous solutions which show deviations from the Onsager equation will either confirm the view that the anomaly between experiment and theory is due to ion association (or incomplete dissociation), or will show that the interionic attraction theory cannot be used at all to account for the behaviour of such solutions. Actually, Bauer's measurements, in the cases for which they have been made, entirely support the view that the deviations observed from the theoretical conductivity curves are due only to the fact that the dissolved solute behaves as a weak electrolyte. The Onsager analysis may not therefore be applied to this group of solutions without some modification. The total number of particles present is less than if complete dissociation took place, and a degree of ionisation must therefore be introduced into the concentration terms (see p. 102).

The results of Hartley's measurements on alcoholic solutions show, too, that in the alkali metal series of salts having the same anion, the tendency of the ions to associate (as represented by the deviations from the square-root law) increases with the atomic number of the metal. Evidently in hydroxylic solvents the higher solvation of the metals of lower atomic number is causing a decreased degree of association due to the increase in the size of the protective sheath of solvent molecules.¹ In nitromethane the relative mobilities of the ions are the same as in the alcohols. Nevertheless the relative tendencies for the ions to associate are in the reverse order to that in the alcohols, which is in agreement with Fajans' rule that the tendency to covalency formation shall be greater, the smaller the cation. Nitromethane and nitrobenzene (in which similar results have been obtained)² are not, like the alcohols, both proton

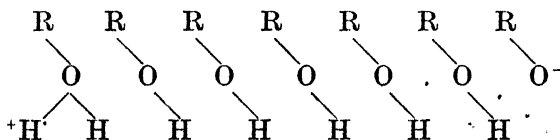
¹ C. P. Wright, Murray-Rust, and Hartley, *J.C.S.* (1931), 199.

² See references, p. 82.

donors and proton attractors. Since they are only proton donors, they will only undergo dipole association with the anions in solution, thus facilitating the association of the anions with the cation.

✓ This theory of the association of electrolytes in different solvents receives further support from the fact that, in hydroxylic non-aqueous solvents, the addition of traces of water greatly reduces the conductivity of an electrolyte, whereas in solvents like nitromethane the reverse effect is observed. In the latter case the addition of traces of water enable the solvate sheath around each ion to be completed preventing, or at least greatly reducing, ionic association, and hence resulting in an increased conductivity.

We may now consider another effect which arises from the physical characteristics of hydroxylic solvents. It is a well-known fact that the hydrion and hydroxyl ion show abnormally high mobilities in their aqueous solutions when compared with the mobilities of other anions and cations. The measurements of the conductivities of acids in hydroxylic non-aqueous solvents show that these ions still have abnormally high mobilities, but that in non-aqueous, non-hydroxylic solvents both ions exhibit a normal type of mobility. This evidence appears to support the Hückel theory for the abnormalities of the mobilities of these ions in water (see p. 359), since the behaviour is not confined to solutions in water, but is extended in a smaller degree to all hydroxylic solvents. Like water, molecules of a hydroxylic solvent are able to associate into long chains in which the relative positions of the molecules are determined by resonance. The liquid therefore has a pseudo-crystalline structure resembling that of water, but the ions are RH_2O^+ and RO^- in place of H_3O^+ and OH^- . These are maintained in position so long as resonance between the possible alternative hydrogen linkages persists.



Each chain therefore forms a zwitterion (see pp. 386 *et seq.*), which cannot contribute to the conductivity. Pure liquids may therefore be expected to have only very small conductivities,¹ and there is adequate experimental evidence which supports this conclusion. Hartley's measurements on the alcohols show that the specific conductivity of "conductivity" methyl alcohol is 0.01×10^{-6} r.o. and that of pure ethyl alcohol, 0.003×10^{-6} r.o. The fact that the mobilities of the ions H_3O^+ and OH^- in water are smaller than the mobilities of the corresponding ions in the alcohols may be attributed to the greater length of the chains in the former case. The length of the chains will, in fact, depend on the equilibrium between the chain-lengthening process which is activated by the evolution of energy for each successive additional molecule, and the chain-breaking process which takes place by thermal agitation.

The most striking feature of non-aqueous solutions of electrolytes is the remarkable influence which minute traces of water may have on the conductivities of the solutions. The effect was first observed by Goldschmidt² on the conductivity and catalytic properties of alcoholic solutions of the hydrogen halides, and since that time the phenomenon has been very fully examined from the experimental point of view.³ The effect may be surprisingly large in some instances. It has been found, for example, that 0.5% of water added to about 0.001N alcoholic solutions of acids decreases the conductivity by 25–30%, although the influence of the water in changing the viscosity and dielectric constant of the medium is not more than about 2%. Such an influence in alcoholic solutions is observed only with the strong acids, and it is therefore attributed to the replacement of the ROH_2^+ ion by the H_3O^+ ion, which, because of its higher proton attractive power, will not lose a proton to the alcohol molecules so easily as the ion ROH_2^+ . When, however, considerable quantities of water are added so that

¹ N. V. Sidgwick, *Ann. Rep. Chem. Soc.*, **31** (1934), 42.

² Goldschmidt, *Z. physikal. Chem.*, **81** (1912), 30 *et seq.*

³ O. L. Hughes and H. Hartley, *Phil. Mag.*, **16** (vii) (1933).

Hartley, Murray-Rust, Macfarlane, and Gatty, *Ann. Rep. Chem. Soc.*, **27** (1931), 339.

the long water chains may be set up, the conductivity again rises, due to the now increased mobility of the hydron. In non-hydroxylic solvents, however, where no such zwitterion chains may be set up, a very different effect is observed. In this case small quantities of water added to the non-aqueous solutions produce large increases in the conductivity. The increase is again out of all proportion to the effect which would be anticipated were the influence merely one of the alteration of the physical constants of the solvent. The addition of only 0.1% of water to a N/500 solution of lithium thiocyanate in nitromethane is sufficient to produce a 65% increase in conductivity, although the decrease in viscosity is only 0.3%.¹ As already explained, this increased conductivity effect is interpreted in terms of the relative tendencies of the ions of electrolytes to associate in non-aqueous solutions.

Although most of the conductivity measurements of electrolytes in non-aqueous solutions have been made using hydroxylic solvents, very interesting results have been obtained from experiments carried out in liquid ammonia and anhydrous hydrogen fluoride. Measurements in these solvents might be expected to give interesting information from what we already know about the mechanism of conduction in solution; for hydrogen fluoride is one of the strongest acids known—that is, it very easily gives up a proton to other substances, so that almost all substances soluble in it will behave as bases or proton acceptors (see p. 366). In liquid ammonia, on the other hand, which is a powerful proton acceptor, almost all substances should behave as acids. Unfortunately very few measurements of the conductivities of salts in liquid ammonia have been made, owing partly to the prominence which has been given to the conductivities of metals in this solvent, but there is a considerable amount of experimental data available for hydrogen fluoride.²

It is surprising to find that in anhydrous hydrogen fluoride,

¹ C. P. Wright, D. M. Murray-Rust, and Hartley, *J.C.S.* (1931), 199.

² Fredenhagen and Cadenbach, *Z. physikal. Chem.*, **145** (1930), 245. J. H. Simons, *Chem. Rev.*, **8** (1931), 231.

organic acids, and even organic compounds, such as acetone, which are normally neutral in water, show conductivities of the same order as that of sulphuric acid (Fig. 30). If, however, it is assumed that, as a strong acid, hydrogen fluoride possesses powerful proton donating properties, the similar conductivities of solutions of water and sulphuric acid in

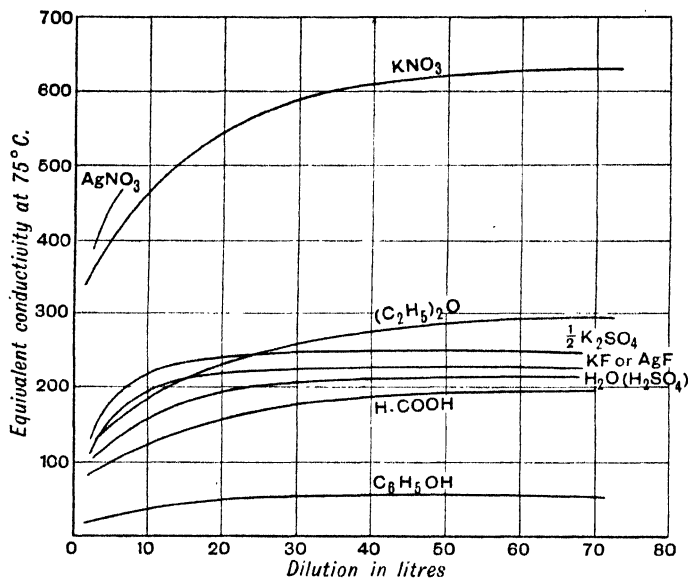
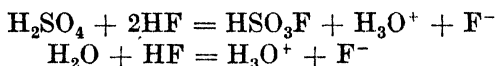


FIG. 30.—CONDUCTIVITIES IN ANHYDROUS HYDROGEN FLUORIDE.

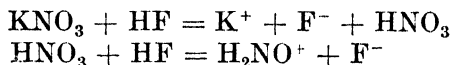
this solvent are at once explained, due to the formation of the same ions



With acetic acid the conductivity of which, although showing the same type of behaviour as water or sulphuric acid, is nevertheless not identical with this, the same number of particles may be expected to be formed. From the difference in conductivity, however, these ions cannot be H_3O^+ and F^- . The acetic acid molecule has acceptor properties, and it may therefore react with hydrogen fluoride as follows :



Trichloroacetic acid, which in water is a stronger acid than acetic acid, and therefore has stronger proton donor and weaker proton attractor properties, is therefore a weaker electrolyte than acetic acid in hydrogen fluoride. Binary salts which are not fluorides show a peculiar behaviour in hydrogen fluoride, as their equivalent conductivities at high dilutions are twice those of the sulphuric acid-water type. They behave therefore as if twice as many particles were present in the solution. This is explained in the same way as the similar effect with the organic compounds, by the reactions



The nitric acid first liberated behaves then like sulphuric acid, as a proton acceptor in the presence of the strongly proton donating hydrogen fluoride molecules.

The insolubility of the other hydrogen halides in anhydrous hydrogen fluoride receives an explanation also in these terms. These compounds, because of their low boiling points and dielectric constants, would be soluble in anhydrous hydrogen fluoride only if they ionised in this solvent. Being, however, only powerfully proton-donating with no proton-attracting properties, they can ionise only in the presence of an acceptor, and hydrogen fluoride is, most of all, not such a compound. Similarly they are unionised in the pure state, a fact which is illustrated by the well-known non-conducting and dielectric properties of pure hydrogen chloride, but immediately a powerful proton acceptor such as water is added, ionisation becomes possible. The conductivity measurements of hydrogen fluoride solutions therefore afford an excellent confirmation of Brönsted's theory of acids and bases which regards these respectively as proton-donating and proton-attracting compounds¹ (see pp. 366 *et seq.*).

Similar measurements of the conductivities of organic substances in liquid hydrogen sulphide confirm these conclusions.² Only the most basic substances, like quinoline,

¹ Brönsted, *Rec. trav. chim.*, **42** (1923), 718.

² W. C. Johnson and A. W. Meyer, *Chem. Rev.*, **8** (1931), 285.

J. W. Walker, J. McIntosh, and E. Archibald, *J.C.S.* (1904), 1098; *Proc. Roy. Soc., A*, **73** (1904), 450.

show any appreciable conductivities in this solvent, for only these can act as proton acceptors from the weakly proton-donating hydrogen sulphide.

Very different results have, however, been obtained from conductivity measurements in liquid ammonia.¹ This solvent has the peculiar property of dissolving many metals to form stable solutions, and the conductivity measurements of these are valuable as a means of investigating the processes taking place during metallic conduction. Strong solutions of the alkali metals in ammonia, for example, are much better conductors than typical salts in the same solvent. At the same time there is no visible deposition in the solution at all, a fact which makes this type of conduction quite analogous to the conduction of electricity through metals. Even in the most dilute solutions colour changes take place round the electrodes during electrolysis, which enable the concentration changes to be followed. It is found that in these solutions, electrolysis is accompanied by all the usual processes, such as the migration of ions, and consequently the changes in the concentration of the solution around the electrodes are observed exactly as if a salt were being electrolysed.

In no case where measurements have been made can any trace of an anode product be found. Kraus² therefore suggests that the ions present are the negative electron and the ordinary positive sodium ion. Both the sodium ion and the electron must of course be solvated for the same reasons as the proton cannot be supposed to exist freely in solution. At higher concentrations the electron is supposed to lose some of its attendant ammonia molecules from the surrounding sheath, and so to travel with higher velocities approaching those with which electrons move in metals. Careful measurements of the conductivities of metal solutions in ammonia show a very sharp increase of the conductivity as the solution becomes more concentrated (see Fig. 31), confirming the increased conductivity of the negative carrier, but as the dilution increases the conduc-

¹ G. A. Kraus, "The Properties of Electrically Conducting Systems," New York, 1922, Chapter XIV.

² C. A. Kraus, *J. Amer. Chem. Soc.*, **36** (1914), 864; **43** (1921), 729.

tivity passes through a minimum and reaches a constant where ionisation is complete. Evidence that there is a common particle in all the metal solutions in liquid ammonia is supplied by the fact that at low concentrations the absorp-

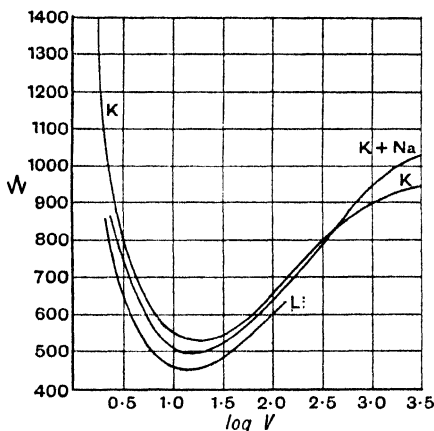


FIG. 31.—CONDUCTIVITIES OF METALS IN LIQUID AMMONIA (Kraus).

tion curves of the solutions of lithium, sodium, potassium, magnesium and calcium are identical.

A quantitative extension of this view that electrons contribute to the conductivity of such solutions has been made by Farkas,¹ by supposing that the mechanism of the conduction by the electrons takes place by quantum mechanical transitions between the neighbouring metal atoms. The influence of the potential gradient will then cause more of these transitions to take place towards the anode than towards the cathode. For an electron in the vicinity of two sodium atoms, the potential energy curve will have the form shown in Fig. 32, where the

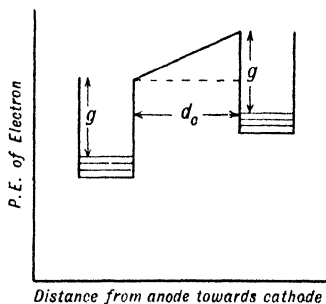


FIG. 32.—POTENTIAL ENERGY DIAGRAM FOR METAL ATOMS IN AMMONIA.

¹ L. Farkas, *Z. physikal. Chem. (A)*, **161** (1932), 355.

drop in potential towards the left is due to the approach of the electron towards the anode. The two troughs represent the two metal atoms, the depth of the highest filled level being the ionisation potential of the atom. The probability of transitions in either direction may be calculated, and from the difference between these the net transitions of electrons towards the anode, and hence the specific conductivity, may be obtained. In order to introduce the concentration of the metal in the solution, it has to be assumed that the atoms occupy positions conforming to a cubic lattice as in the solid, the distance d_c of the atoms from one another depending on the concentration. The curve so obtained for the variation of the conductivity with concentration agrees well with the experimental data despite the simplifying assumptions which have to be made.

The Bjerrum and Fuoss Generalised Theories of Conductivity.

Although the conductivities of aqueous solutions have been considered earlier in this chapter at some length, because water is the commonest solvent used in chemical work, aqueous solutions represent only a limiting case. The dielectric constant of water is more than twice as great as that of any other common solvent, and any conclusions reached from measurements in aqueous solutions therefore cannot be assumed necessarily to apply to other solutions. On the other hand, any theory which can explain the observed effects in non-aqueous solutions will very probably apply, at a much higher concentration, to aqueous solutions. As has already been explained, in non-aqueous solvents, especially those which are non-hydroxylic, ionic association will occur at very low concentrations indeed, since the decreased dielectric constant increases the interionic forces. The Onsager treatment which assumes that complete dissociation has taken place will therefore fail to represent the experimental results in non-hydroxylic solutions even at quite low concentrations, and a more generalised theory of conductivity which will include these special cases is desirable.¹

¹ R. Fuoss, *Chem. Rev.*, 17 (1935), 27.

Bjerrum proposes, for the general case, to divide interionic effects into two types: long- and short-range. The former he supposes to be of the type occurring in a completely dissociated electrolyte solution, the latter to represent the agglomeration of ions into ion pairs, etc., under the influence of Coulomb attractions, which may be treated by the methods of the ordinary dissociation theory.¹ The ion pairs are associated in the sense that they approximate to solute particles and they have only a dipole external field. This contributes very little to the total potential energy of the solution by comparison with the forces due to ion-ion attractions.

Ions which are farther apart than a certain critical distance q defined as

$$q = \left| \frac{z_i^2 e^2}{2DkT} \right| \quad . \quad . \quad . \quad (62)$$

cannot be considered as associated, and these interact with all the neighbouring ions, and not merely with the nearest ion as in the ion pairs. Now, the potential energy of an ion with respect to the nearest unpaired ion is small compared with the energy of thermal agitation. The potential energies of these ions will therefore be given approximately by the Boltzmann-Poisson equation of the Debye-Hückel theory.

Fuoss has made Bjerrum's views more definite by showing that the artificial separation of the ions into ion pairs and unpaired ions has a physical basis provided the ion pair is defined in a certain way.² This convention is as follows. Every ion is supposed to be paired with an ion of the opposite charge. A negative ion lying within a spherical shell of thickness dr at a distance r from a given positive ion forms an ion pair with this, provided no other unpaired negative ion is present within the sphere of radius r (volume V). We may now calculate the distribution $G(r)$ of the ion pairs with the distance. Putting $G(r)dr$ as the probability of the positive ion forming a pair with one of the N negative

¹ N. Bjerrum, *Kgl. Danske Videnskabs. Selskab.*, 7 (1926), No. 9. *Ergeb. Exack. Nat.*, 6 (1926), 125.

See also R. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, 55 (1933), 1019; and R. Fuoss, *Chem. Rev.*, 17 (1935), 27.

² Fuoss, *Trans. Faraday Soc.*, 30 (1934), 967.

ions inside the shell contained between the spheres r and $r + dr$, then $G(r)$ is proportional to N , to $\frac{4\pi r^2 dr}{V}$ and (neglecting screening effects) to the Boltzmann factor $\exp\left(\frac{e^2 z_i^2}{DkTr}\right)$ and to the probability $f(r)$ that an unpaired negative ion is not already inside the sphere of radius r . But from the definition of $G(r)dr$ we may evaluate $f(r)$, for $G(x)dx$ is the probability that a negative ion shall be found within the range $x < r \leq x + dx$, and $G(r)$ is the probability that no such ion shall be found in the sphere $\frac{4\pi r^3}{3}$. Thus

$$f(r) = 1 - \int_a^r G(x)dx. \quad (63)$$

where a is the ionic radius or, more strictly, the distance of closest approach of the positive and negative ions. Hence we have

$$G(r)dr = \frac{4\pi N}{V} r^2 dr \exp\left(\frac{e^2 z_i^2}{DkTr}\right) \left\{1 - \int_a^r G(x)dx\right\} \quad (64)$$

or, substituting for q from (62)

$$G(r)dr = \frac{4\pi N}{V} r^2 dr e^{\frac{2q}{r}} \left\{1 - \int_a^r G(x)dx\right\} \quad (65)$$

For small values of r , $G(r)dr$ reduces to the average number of ions of the opposite charge—i.e. :

$$G(r) \approx \frac{4\pi N}{V} r^2 e^{\frac{2q}{r}} \quad (66)$$

Using this condition we have :

$$G(r)dr = \frac{4\pi N}{V} r^2 \exp. G \left[\frac{2q}{r} - \frac{4\pi N}{V} \int_a^r x^2 e^{\frac{2q}{x}} dx \right]. \quad (67)$$

$G(r)$ therefore has stationary values when

$$\frac{2}{r} - \frac{2q}{r^2} - \frac{4\pi N}{V} r^2 e^{\frac{2q}{r}} = 0 \quad (68)$$

It can readily be shown that, for dilute solutions where $q \ll \left(\frac{V}{N}\right)^{\frac{1}{3}}$, but $q > a$, that a minimum occurs at

$$r \approx q \quad (69)$$

and a maximum at

$$r \simeq \left(\frac{V}{2\pi N} \right)^{\frac{1}{3}} = \rho \quad . \quad . \quad . \quad (70)$$

A plot of the function $G(r)$ for specific values of the characteristic distances occurring in the final expression is exhibited in Fig. 33. At A where $r \simeq q$ there are very few ion pairs compared with the numbers at C and B , and it is therefore quite justifiable to divide the ions into two classes by a critical radius q . But whereas Bjerrum regards ions separated by a greater distance than q as "free" ions, Fuoss calls them long-range ion pairs. Both authors, however, propose that they should be treated in exactly the

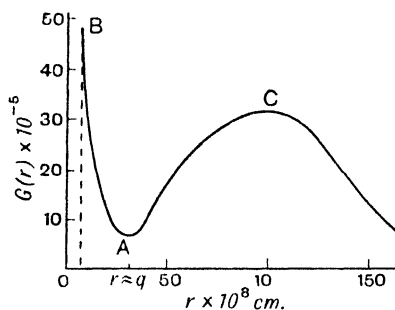


FIG. 33.—THE DISTRIBUTION FUNCTION $G(r)$ (Fuoss).

same way as Debye and Hückel adopted for their model—*i.e.* the Poisson-Boltzmann equation may be used to calculate their energies.

The conductivity of a solution for which the Fuoss-Bjerrum model is adopted may be calculated as follows. If a fraction $1 - \alpha^*$ of the solute is supposed to be associated and therefore non-conducting, the total current for unit potential between unit electrodes is

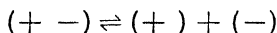
$$i = Fc\alpha^*(\lambda_+ + \lambda_-) \quad . \quad . \quad . \quad (71)$$

where c is the equivalent concentration per c.c. and α^* is the true degree of dissociation—*i.e.*, the proportion of ions in the long-range pairs to the total number of particles present in the solution. The mobilities of the free ions, which are due to the long-range interionic forces, are given

by Onsager's equation $\lambda = \lambda_{\infty} - A\sqrt{c}$, and therefore the equivalent conductivity is, from its definition,

$$A = \alpha^*(\lambda_{\infty} - \alpha\sqrt{c\alpha^*}) \quad . \quad . \quad (72)$$

where α is the Onsager coefficient.¹ Since in this equation it is supposed that both the actual number of particles present and their mobilities change with concentration, it combines the dissociation theory of Arrhenius with the conception that electrostatic attraction is an important factor in determining the conductivity of solutions. From this equation it is possible to calculate α^* as a function of the concentration, but this does not furnish a test for the equation (see below). In order to verify equation (72) experimentally, it is necessary to introduce another relation between α^* and the concentration. Now, assuming an equilibrium between free ions (long-range ion pairs) and the short-range or associated ion pairs,



which is controlled by the balance between the Coulomb forces (operating in the ion pairs) and thermal agitation governing the free ions, the mass law gives,

$$\frac{[+][f_+][-]f_-}{[+ -]f_{+-}} = \frac{c\alpha^{*2}f^2}{1 - \alpha^*} = K \quad . \quad . \quad (73)$$

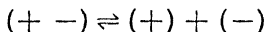
since the assumption that the neutral molecules are present in dilute solution is equivalent to writing $f_{+-} = 1$, and it may further be assumed that $f_- = f_+$. The square brackets are used to denote concentrations, and the activity coefficients of the free ions are here introduced to account for the long-range interionic attractions. The concentration of free ions is $c\alpha^*$ and the value of f is therefore given from equation (320), by omitting the "salting out" term

$$-\ln f = \frac{\beta\sqrt{c\alpha^*}}{1 + \delta\sqrt{c\alpha^*}}$$

The value of K , the equilibrium constant between the free ions and the ion pairs, may be calculated theoretically from

¹ This α , the first Onsager coefficient, must not be confused with α^* , the true degree of dissociation.

the distribution function, for, as the concentration is decreased, this function undergoes a transition from short-range to long-range ion pairs which is equivalent to a shift in the equilibrium (constant K):



The activity coefficient f refers only to free ions—*i.e.*, to long-range ion pairs, and the Debye-Hückel approximation

$$\frac{e\psi}{kT} \ll 1$$

which makes the Boltzmann-Poisson equation linear, may be applied. Thus:

$$-\ln f^2 = 2\beta' \sqrt{c\alpha^*} \quad . \quad . \quad . \quad (74)$$

and substitution therefore for f^2 and for α^* from (73) and (74) in equation (72) gives, after rearrangement:

$$\frac{F}{A} = \frac{1}{KA_\infty^2} \frac{cAf^2}{F} + \frac{1}{A_\infty} \quad . \quad . \quad . \quad (75)$$

This equation therefore shows how the conductivity varies with the concentration after allowing for the formation of ion pairs as the concentration increases.

There are only two arbitrary constants in the equation, f and K , and two points will therefore determine the conductivity curve. Kraus and Fuoss have verified the equation for a number of non-aqueous solutions.¹ Their results (Fig. 34) show that, together with the limiting law of Onsager (the limiting Onsager slopes are given in the figure), the method of Fuoss, allowing for the two types of interionic forces, predicts, with quite a high degree of certainty, the conductivities of electrolytes in dilute solutions. The range of application of the theory depends on the magnitude of the dielectric constant of the medium—*i.e.*, on the relative magnitude of the interionic attractions.

In concentrated solutions, however, there is no reason why more complicated agglomerations of ions should not occur. Freezing-point measurements of molecular weights support the view that in solvents of low dielectric constant complex association increases rapidly with rise in the

¹ Kraus and Fuoss, *J. Amer. Chem. Soc.*, **55** (1933), 476.

concentration.¹ At higher concentrations, therefore, there is probably a much larger proportion of short-range ion pairs and the probability of a free ion being close to a short-range pair is much increased. This in turn increases the chance of a stable three-ion group being present. The probability of this occurrence increases as the concentration

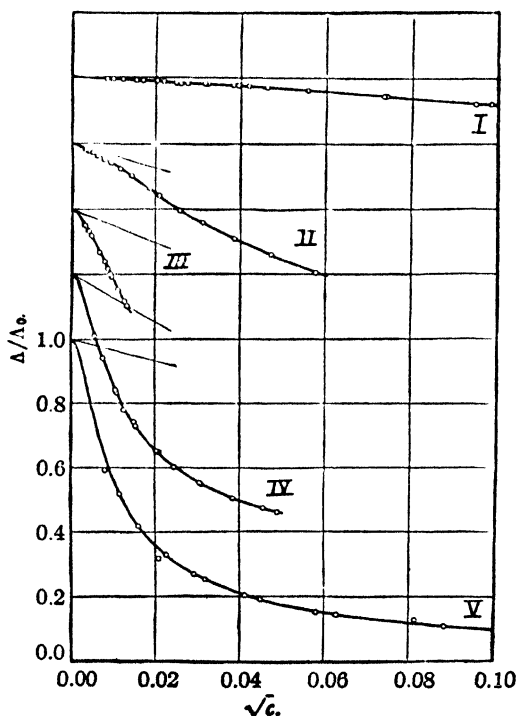
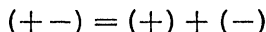
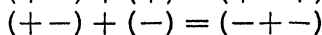
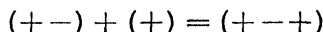


FIG. 34.—COMPARISON OF CONDUCTIVITY DATA IN NON-AQUEOUS SOLUTIONS.

risers and as the dielectric constant falls.² In addition to the equilibrium



there will therefore be the equilibria



¹ Kraus and Vingee, *J. Amer. Chem. Soc.*, **56** (1934), 511.

² Fuoss and Kraus, *ibid.*, **55** (1933), 2387.

each with a separate dissociation constant. The effect of the free ions remaining may be allowed for by introducing their activity coefficients, and the conductivity may then be calculated as in the above case.

Very few observations have been made with solutions in which these conditions exist, but the theory accounts for the minimum which occurs in the conductivity curves of electrolytes in solvents with dielectric constants under 10, and it gives an explanation of the shift of this minimum towards higher concentrations with an increase in the dielectric constant.

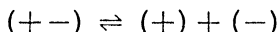
It should be emphasised, however, that the physical picture of ion association which Fuoss uses in his theory of conduction is not original. As has already been pointed out, Bjerrum¹ assumed that the formation of ion pairs (corresponding to Fuoss' short-range pairs) took place only between fully solvated ions without any appreciable deformation of the electron orbits, and therefore without the formation of any permanent chemical linkage. In a sense, therefore, the *physical* assumptions made by Fuoss are only an extension of the ideas of Bjerrum.

It appears therefore that the behaviour of dilute solutions of strong electrolytes may be divided into three classes. Firstly, over a very small range near infinite dilution the electrolyte may be assumed to be completely dissociated into free ions and the properties are accounted for accurately by the Onsager equation. This range extends to 0.001N for the particular case of aqueous solutions because of the high dielectric constant of water. Secondly, at concentrations above this, association is supposed to take place by the formation of ion pairs and triple ion groups which may be treated by the Arrhenius theory like weak electrolytes in water. The properties can only be predicted on these assumptions if the concentration is not too high. At high concentrations, however, ion associations will be present of types too complicated to be treated by the present methods of mathematical analysis. For this reason, no advance has yet been made towards solving the general problem of strong solutions of strong electrolytes.

¹ Bjerrum, *Ergebnisse Exact. Nat.*, 6 (1926), 125.

The "True Degree of Dissociation" of Electrolytes.

There are a few cases in which the Raman spectra of the solutions (*e.g.*, of the mineral acids) do show that definite molecule formation with true chemical linkage does occur when the concentration is appreciable. In the majority of cases, however, the evidence seems to show that group association of the ions takes place with the formation of only electrostatic linkages between the ions. For example, the evidence from the absorption spectra of the alkali and alkaline-earth chlorides in solutions,¹ and from the constancy with changes of concentration of the extinction coefficients of certain salts in dilute non-aqueous solutions² supports the conclusion that here there has been no permanent molecule formation. If therefore only temporary ion group association between any number of given ions occurs, the degree of dissociation will not necessarily represent the extent to which a given equilibrium, *e.g.*



moves to the right. On the contrary, it will only be an arbitrary number representing the extent of the association of different types. Only the Arrhenius degree of dissociation can express the magnitude of the simple dissociation, and our number must therefore be distinguished from this by calling it the "true degree of dissociation."

Fuoss³ has obtained a formal expression for this "true degree of dissociation" by solving equation (72) by means of a suitable transformation—viz.

$$z = \alpha A_{\infty}^{-1} \sqrt{cA} \quad . \quad . \quad . \quad (76)$$

Then it is found that

$$A = \alpha^* A_{\infty} F(z) \quad . \quad . \quad . \quad (77)$$

where

$$F(z) = 1 - z(1 - z(1 - z(1 - z \dots)^{-1})^{-1})^{-1} \quad (78)$$

Equation (77), however, is not capable of experimental verification, since there is no method for measuring α^* experimentally.

¹ S. Schiebe, *Z. Electrochem.*, **34** (1928), 497.

² H. von Halban and L. Ebert, *Z. physikal. Chem.*, **112** (1924), 321.

³ R. Fuoss, *J. Amer. Chem. Soc.*, **57** (1935), 488.

A somewhat different procedure has been adopted by Davies¹ and Wien² for the calculation of α^* . The molecular conductivity is given by

$$\Lambda = \alpha^*(\lambda_+ + \lambda_-) \quad . \quad . \quad . \quad (79)$$

or, denoting by Λ_x , the sum of the mobilities of the ions at the given concentration, by

$$\Lambda = \alpha^*\Lambda_x \quad . \quad . \quad . \quad . \quad (80)$$

Now, Λ_x may be found from equation (40) provided the concentration term for free ions is substituted, *i.e.*

$$\Lambda_x = \Lambda_\infty - (\alpha\Lambda_\infty + \beta)\sqrt{c\frac{\Lambda}{\Lambda_x}} \quad . \quad . \quad (81)$$

From equation (80) α^* may now be calculated by a series of successive approximations by first calculating Λ_x assuming $\alpha^* = 1$, using this value to find α^* , and so calculating a new value of Λ_x and repeating the process. Measurements of the conductivities of formic acid in water at 18° give by this method $\alpha^* = 0.0764$ when $c = 0.03208$. Alternatively, Λ_x may be found as one of the roots of the cubic equation (81) (Wien), and calculations made by this method on the strongly associated solutions of lithium bromide in acetone show that over the whole concentration range where calculations are possible, the true degree of dissociation is greater than the Arrhenius function. Unfortunately, since all these methods for calculating the true degree of dissociation have at some stage used the Onsager equation, they can only be applied over ranges of concentration to which Onsager's analysis applies. For non-aqueous solutions the range of application is therefore particularly limited, and another difficulty arises in these cases, since the Λ_∞ values are not accurately known.

A further method which may be of some value in estimating the true degree of dissociation depends on the effect observed by Debye and Falkenhagen that the presence of ions in a pure solvent changes the dielectric constant in

¹ C. W. Davies, *Trans. Faraday Soc.*, **23** (1927), 351.

² See Falkenhagen, "Electrolytes," trans. R. P. Bell, Oxford (1935), pp. 308 *et seq.*

accordance with a square-root law.¹ The effect is only small and is difficult to measure—indeed, impossible at high concentrations—but calculations have been made in the case of lithium bromide in acetone by comparison with potassium iodide which is almost completely dissociated in this solvent. The results calculated at two concentrations give

$$\begin{array}{ll} \text{for } c = 0.0069 & \alpha^* = 0.33 \\ \text{for } c = 0.069 & \alpha^* = 0.29 \end{array}$$

and these agree fairly satisfactorily with Wien's calculations by the above method, considering the practical difficulties in making the dielectric constant measurements.

The Dispersion of Conductivity with Frequency.

We now have to consider two very important effects: the change of conductivity with the frequency (dispersion of conductivity) and the Wien field effect which is the change in conductivity with increasing field strengths. Neither of these can be explained by a simple dissociation theory, and while the Wien effect was first observed experimentally and later explained in terms of the ion atmosphere theory, the dispersion of conductivity with frequency was predicted from the theory and later investigated experimentally.²

In an alternating field, the frequency of which is very large compared with the relaxation frequency ($1/\tau$) of the ion atmosphere, there will be no unsymmetrical distribution of the ion atmosphere, for its formation requires a time interval of the same order as the time of relaxation. The dissymmetry retarding effect on the ion will therefore disappear. Thus with increasing frequency of the applied field the dissymmetry term in the expression for the conductivity decreases and the equivalent conductivity Λ increases where,

$$\Lambda = \Lambda_{\infty} - \Lambda_I - \Lambda_{II} \quad . \quad . \quad . \quad . \quad . \quad (82)$$

¹ Debye and Falkenhagen, *Physikal. Z.*, **29** (1928), 423. Special case for stationary fields.

² Debye and Falkenhagen, *Z. Electrochem.*, **34** (1928), 562; *Physikal. Z.*, **28** (1927), 836.

Falkenhagen and Williams, *Chem. Rev.*, **6** (1929), 317.

The dispersion effect may be represented by the ratio of the values of Λ_1 at a field frequency ω to its value when the field frequency, is zero. Since the time of relaxation is inversely proportional to the concentration there should, for a given frequency, be a certain concentration for which the increase in the equivalent conductivity due to the dispersion is a maximum. The presence of this maximum was verified by Sack, who showed also that the observed rise in conductivity,

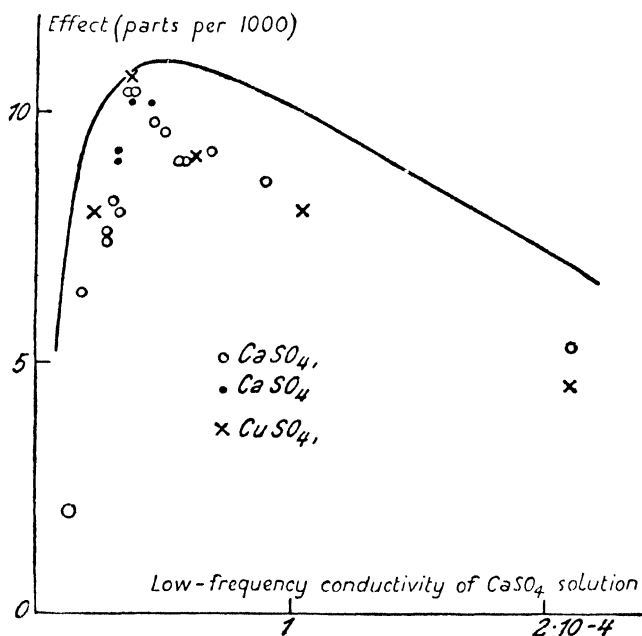


FIG. 35.—DISPERSION OF CONDUCTIVITY WITH FREQUENCY FOR CaSO_4 AND CuSO_4 (Deubner).

as the frequency of the field increased, was of the order predicted by the theory. More accurate measurements have been made by employing a null method¹ instead of using the damping effect caused by the electrolyte solution, as in Sack's apparatus. An ordinary valve transmitter containing the electrolytic resistance in parallel with a variable condenser to give reaction, was arranged to be just

¹ A. Deubner, *Physikal. Z.*, **30** (1929), 946; *Ann. Physik*, **5** (v) (1930), 305; *Physikal. Z.*, **33** (1932), 223.

on the point of oscillation. Here the intensity of oscillation measured by galvanometer deflections in a receiving circuit changes very rapidly for small changes in the resistance of the electrolyte. Small changes in the dielectric constant due to the dispersion effect are negligible near the maximum intensity of oscillation, and by flowing different electrolytes into the cell one after another, measurements of the high-frequency conductivity for different solutions could be made accurately without disturbing the constancy of the oscillation frequencies. At all concentrations at which the dispersion effect has been measured it is found to be positive (Fig. 35), agreeing with the interionic attraction theory, while over the limiting range of high dilutions, to which the theory of dispersion applies accurately, the results are in approximate quantitative agreement with the theory (see Fig. 35).

Field Effects on the Conductivities of Electrolytes.

The Wien field effect does not become apparent until the field strengths are some 10^5 times those ordinarily employed for conductivity measurements.¹ With these high fields, however, the remarkable effect is found that the conductivity and the applied field are no longer related by Ohm's law. In the experimental apparatus for observing conductivities under high fields the high current densities are applied only for very short intervals of time during the measurements, otherwise the heating and electrolysis effects on the solution become enormous. The difficulties of doing this were overcome by Wien and Malsche by charging up a condenser K and subsequently discharging it through a spark gap F in the apparatus (Fig. 36).² The potential could be increased by widening the spark gap and the minimum resistance balanced against a known variable resistance by means of the barretter bridge coupled inductively with the two branches of the oscillation circuit L_1 and L_2 . The barretter bridge is a device by which the dissymmetry in the oscillation circuit may be detected. It

¹ Wien, *Ann. Physik.*, **83** (1927), 327.

² M. Wien and J. Malsche, *ibid.*, **83** (1927), 305.

consists of two small resistances r_1 and r_2 , the sum of which remains constant but the ratio of which may be varied as in Poggendorff's compensation method for comparing E.M.F.'s. These two resistances form two arms of the bridge, the other two arms consisting of two matched lamp-bulbs. The high-frequency current is confined to the bulbs by the coils S , the high-frequency capacities of which are very large compared with that of the bulbs. Connection with the coupling coils to the oscillation circuit is made through the condensers k_1, k_2 . The bridge is operated from one or

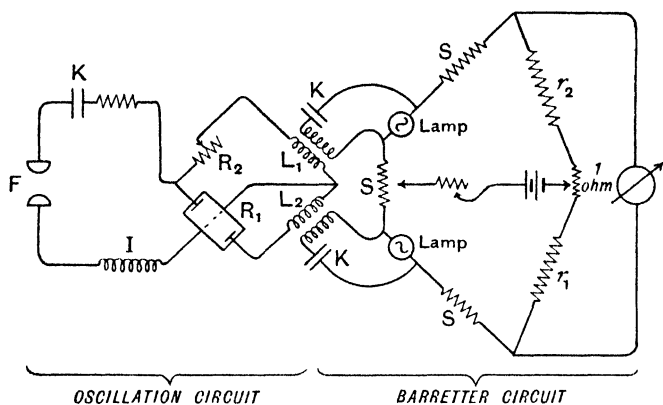


FIG. 36.—WIEN-MALSCHÉ METHOD FOR OBSERVING THE FIELD EFFECT.

two accumulators and the balance point observed on the galvanometer in the usual way. The lamp resistances show equal heating when the bridge is balanced only if the oscillation circuit is entirely symmetrical. If the resistance R_2 is therefore balanced when the electrolyte resistance is in the oscillation circuit, there will be no deflection of the galvanometer. If now the electrolyte resistance is replaced by a variable resistance which is again adjusted to the balance point, the resistance of the electrolyte will be equal to that of the variable resistance.

Although observations using very high fields can only be made with very dilute solutions, the important conclusion emerges that the conductivity approaches a limiting value as

the field becomes more intense (Fig. 37). This result was predicted from the Debye theory. If the field strength is too high, however, the ionic velocities may reach such high values that Stokes' law can no longer be applied with accuracy. The slope of the conductivity-potential gradient curve as this limiting condition is approached is greater the more dilute the solution, thus confirming the theoretical predictions in a remarkable fashion. For at the highest field strengths, where the velocities of the ions become of the order of one metre per second, the ion will move through

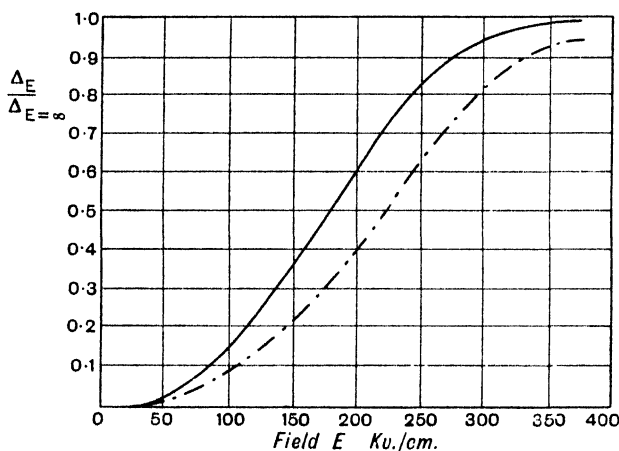


FIG. 37.—THE WIEN FIELD EFFECT.

many times the thickness of its atmosphere during the time of relaxation required to restore the spherically symmetrical distribution. The limiting value of the conductivity in very high fields corresponds therefore, like the conductivity at very high frequencies, to a state in which the ionic velocities are independent of the ion atmosphere, and therefore of both the disymmetry and the electrophoretic effects. The limiting value of the conductivity $\Lambda = \Lambda_{\infty}$ obtained in this way could be used to estimate the true degree of dissociation at the concentration of the electrolyte taken in the particular determination. Such an estimation could, however, be made only for the case of strong electrolytes. For weak electrolytes the variation

of conductivity with field strength is many times more rapid than for strong acids, and the effect is much too great to be attributed to the properties of the ion atmosphere like the normal field effect and the dispersion of the conductivity with frequency.¹ In weak salts and acids there must therefore be some other superposed effect, arising from quite different physical causes, and which results in a greatly decreased number of molecules and an increased degree of ionisation.

This "dissociation field effect" which gives rise to the anomalous observed effect in these weak electrolytes should obviously reach saturation with complete dissociation. Actually, however, this is never observed, and Wien has expressed the view that complete dissociation is prevented by the rapid recombination of the ions. The difficulty of separating the normal and dissociation field effects, which operate together in weak electrolytes, renders it impossible at present to estimate the true degree of dissociation from the anomalous field effect.

Onsager has shown that, adopting Bjerrum's convention for the definition of ion pairs, a detailed study of the mutual approach and parting of the components of these ion pairs may be made by assuming that they are governed by the laws of thermal agitation.² It is found that the rate constant for the dissociation of the ion pairs is increased with an increase of the field in such a way that, for all except the lowest and highest field intensities, the increase in dissociation is directly proportional to the field strength. The rate may be computed theoretically by assuming that recombination proceeds just as frequently as the ions approach one another under the Coulomb forces. Experimental results for a number of weak electrolytes in various solvents show that these predictions are, on the whole, confirmed except at quite low field strengths.³ Much of the experimental work, however, was done to investigate the general field effect rather than to supply evidence for the increased dissociation of weak electrolytes.⁴ Consequently

¹ M. Wien and J. Schiele, *Physikal. Z.*, **32** (1931), 515.

² Onsager, *J. Chem. Phys.*, **2** (1934), 599.

³ J. Schiele, *Ann. Physik.*, **13** (v) (1932), 811.

⁴ G. Bauer, *ibid.*, **6** (v) (1930), 253.

in many of the cases which have so far been investigated there are no accurate data for the dissociation constants in question, and it is difficult to find more than the qualitative trend of the dissociation field effect in these cases. In non-aqueous solutions, any complications due to a variation with the applied field of the degree of dissociation are removed. In these cases the dissociation is very small and the majority of electrolytes show the linear variation of conductivity with field intensity which represents one of the limiting cases of the general theory.

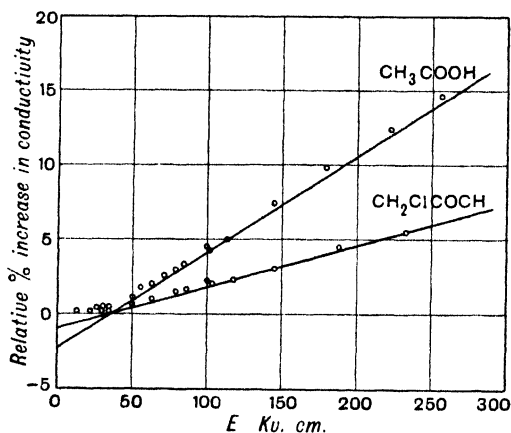


FIG. 38.—THE DISSOCIATION FIELD EFFECTS IN ACETIC ACIDS.

Apart from the dissociation field effect in very intense fields for strong electrolytes and in much more moderate fields for weak electrolytes, the dispersion effect and the normal field effect (Wien effect) are quite parallel in form and magnitude. Both effects depend solely on the relative ease with which the ion atmosphere is formed, but the dissociation field effect is quite different in character, and as soon as it becomes appreciable the parallelism between the dispersion and field effects disappears. Since both the dispersion and the normal field effects are direct consequences of the existence of the ion atmosphere, their prediction and quantitative interpretation in terms of the Debye-Hückel theory provide the most conclusive evidence for the theory

of interionic attraction. But while the new theory is now universally accepted, it has not entirely displaced the Arrhenius view of ion dissociation, but it has revised and extended the earlier views, and has enabled a quantitative prediction to be made of much of the observed behaviour in strong electrolytes over the concentration ranges where the physical assumptions made are plausible.

CHAPTER IV

TRANSPORT NUMBERS AND IONIC MOBILITIES

THE mobilities and transport numbers of ions are both closely related to the conductivity. They depend on the same irreversible processes that take place when an external electric field is applied to an electrolyte solution, and they will therefore show a similar dependence on the concentration. Changes in the concentration of the solutions surrounding electrodes, during electrolysis, were first observed by Faraday. Later, in 1835, Gmelin demonstrated that oppositely charged ions generally moved with different velocities under the same applied field, and Hittorf made the first accurate measurements of the concentration changes which took place.¹ The explanation of the phenomenon was not put on a satisfactory basis, however, until Kohlrausch in 1875 formulated the law of independence of mobilities.

It had been observed that the conductivities at infinite dilution of many series of salts containing a common ion showed a constant difference. The following conductivity values at 18° C. (taken from recent measurements) for sodium and potassium salts having a common ion, illustrate this :

KCl = 130.10	NaCl = 108.99	Difference = 21.11
KNO ₃ = 126.56	NaNO ₃ = 105.33	Difference = 21.23
KIO ₃ = 98.49	NaIO ₃ = 77.42	Difference = 21.07

This constant difference observed between different salts of the same two cations or anions led Kohlrausch to suppose that the conductivity of an electrolyte at infinite dilution was

¹ Hittorf's papers published in *Poggendorff's Annalen* have been collected in No. 23 of Ostwald's "Klassiker der Exakten Wissenschaften."

the sum of the partial limiting conductivities $(\lambda_+)_\infty$, $(\lambda_-)_\infty$ of the separate ions. This may be expressed by the equation

$$\Lambda_\infty = (\lambda_+)_\infty + (\lambda_-)_\infty \quad . \quad . \quad . \quad (83)$$

The mobilities of the ions are defined as their velocities under unit potential gradient, and they will not therefore be the same as the partial ion conductances.

If in a solution of an electrolyte, the potential gradient is represented by G , and v_- and v_+ denote the respective velocities of the anion and cation under unit potential gradient—i.e., their mobilities—then

$$\text{velocity of anion} = v_- G$$

$$\text{velocity of cation} = v_+ G$$

The charge carried by the anions is equal to $N_1 z_1 e$, where N_1 is the total number of anions discharged each of valency z_1 and e is the ionic unit charge. A similar expression $N_2 z_2 e$ gives the total charge carried by the cations, and since the current is given by the product of the charge and the velocity,

$$\begin{aligned} \text{current density due to the anions} &= N_1 z_1 e G v_- \\ \text{current density due to the cations} &= N_2 z_2 e G v_+ \\ \text{total current passing} &= e G (N_1 z_1 v_- + N_2 z_2 v_+) \end{aligned} \quad (84)$$

Since on the whole the solution is electrically neutral and there is no accumulation of charge at any point within it, we may write :

$$N_1 z_1 = N_2 z_2 \quad . \quad . \quad . \quad (85)$$

and the total current passing is therefore $N_1 z_1 e G (v_1 + v_2)$. The fraction of the current carried by the anions will be

$$\frac{N_1 z_1 e G v_-}{N_1 z_1 e G (v_- + v_+)} = \frac{v_-}{v_- + v_+} = n_- \quad . \quad (86)$$

and similarly the fraction of the current carried by the cations is $v_+ / (v_- + v_+)$. These expressions are known as the transport numbers of the respective ions.¹ Since the

¹ In the case of mixed electrolytes, Hittorf supposed that the ions present carried the current in the ratio of their conductivities, and this view has been confirmed substantially by experiment (D. A. MacInnes and J. Dewey, *J. Amer. Chem. Soc.*, **48** (1925), 1922; *ibid.*, **49** (1927). M. Taylor, *ibid.*, **48** (1926), 599).

transport numbers are therefore functions of the velocities of the ions, ionic transport must be classed as an irreversible process, like conductivity.

From the definition of transport numbers it is evident that the sum of the transport numbers for two ions in any solution will be unity. Knowing the transport number for one ion, that for the other may therefore be calculated. The relation

$$n_+ + n_- = 1 \quad . \quad . \quad . \quad (87)$$

in any solution of an electrolyte, has been tested by using the most accurate independent data available, and has been found to hold in every case within the limits of experimental error.¹

Variations of Transport Numbers with Concentration.

The interionic theory predicts that the mobilities, and therefore the transport numbers, should vary both with their valencies and their concentrations. Since, however, the expressions for the transport numbers involve a ratio of mobilities, they vary only slightly with concentration, and very accurate experimental methods must be used to detect this variation. The results which have been obtained by the very accurate moving-boundary method show that the Onsager theory applied to the transport numbers of ions is confirmed over the limiting range. On the other hand, the Arrhenius dissociation theory supposed the mobilities of the ions (and therefore their transport numbers) to be independent of the concentrations, only the numbers of ions present in the solution varying with the concentration. Some of the early measurements by analytical methods (see p. 120) did show a small variation of the transport number with the concentration, but this was attributed at the time to complex ion formation in the solution.²

Unfortunately, as with conductivity measurements, observations of the transport numbers and mobilities of ions cannot be made at or very near infinite dilution where information about the limiting mobilities of the ions is

¹ MacInnes and Longworth, *Chem. Rev.*, **11** (1932), 212.

² B. Steele, *Phil. Trans. (A)*, **198** (1902), 105.

desirable. But if an expression can be obtained which relates the transport number to the concentration over a wide range, it should be possible to estimate the limiting values of the transport numbers by extrapolation. An empirical equation between the transport number and the concentration was first proposed by Grinnell Jones and Dole:¹

$$n = \frac{k_1}{1 + k_2\sqrt{c}} - 1 \quad . \quad . \quad . \quad (88)$$

in order to obtain values of the transport numbers from measurements of the E.M.F.'s of concentration cells. Although this equation interprets the variations of transport number with concentration with fair accuracy at moderate concentrations, it does not extrapolate to infinite dilution with the correct limiting slope. According to the Onsager analysis, the equivalent conductivity at a dilution c within the limiting range is given by equation (40):

$$\Lambda = \Lambda_\infty - (\alpha\Lambda_\infty + \beta)\sqrt{c}$$

Now, by definition, the transport number (of the cation) is given by:

$$\begin{aligned} n_+ &= \frac{v_+}{v_+ + v_-} = \frac{\lambda_+}{\lambda_+ + \lambda_-} \\ &= \frac{(\lambda_+)_\infty - [\alpha(\lambda_+)_\infty + \beta]\sqrt{c}}{(\lambda_+)_\infty + (\lambda_-)_\infty - [\alpha\{(\lambda_+)_\infty + (\lambda_-)_\infty\} + 2\beta]\sqrt{c}} \quad (89) \end{aligned}$$

where the λ 's represent the ionic conductivities at the concentration c . At infinite dilution the transport number is, from equation (86):

$$(n_+)_\infty = \frac{(\lambda_+)_\infty}{(\lambda_+)_\infty + (\lambda_-)_\infty} \quad . \quad . \quad . \quad (90)$$

and therefore substituting from (89)

$$n_+ = (n_+)_\infty - \frac{1 - 2(n_+)_\infty}{\Lambda_\infty - (\alpha\Lambda_\infty + 2\beta)\sqrt{c}} \beta \cdot \sqrt{c} \quad . \quad (91)$$

where Λ_∞ is the equivalent conductivity at infinite dilution of the electrolyte. Since we have assumed the validity of Onsager's equation, equation (89) will therefore predict the

¹ G. Jones and M. Dole, *J. Amer. Chem. Soc.*, **51** (1929), 1073. G. Jones and Bradshaw, *ibid.*, **54** (1932), 138.

values for the transport number correctly, within the limiting range of high dilutions to which the Onsager treatment may be applied without sensible error.¹ It gives for the limiting slope of the variation of transport number with concentration :

$$\left(\frac{\partial n_+}{\partial \sqrt{c}}\right)_{c \rightarrow 0} = \frac{[2(n_+)_{\infty} - 1]\beta}{A_{\infty}} \quad . \quad . \quad . \quad (92)$$

Equation (91) allows an extrapolation to be made from concentrations where measurements are possible to infinite dilution. The results obtained for the limiting transport numbers when combined with the experimental limiting conductivities give values for the limiting individual ion conductivities.² For by Kohlrausch's law

$$(n_{\pm})_{\infty} = \frac{(\lambda_{\pm})_{\infty}}{(\lambda_{+})_{\infty} + (\lambda_{-})_{\infty}} = \frac{(\lambda_{\pm})_{\infty}}{A_{\infty}} \quad . \quad . \quad (93)$$

As the values for $(\lambda_{\pm})_{\infty}$ using this equation may be obtained from measurements in a series of electrolytes, they do not depend on only one transport-number measurement. Transport-number determinations may be made, over a range of low concentrations, almost as accurately as measurements of the conductivity and the fact that the same values of λ_{∞} are obtained for an ion when measurements are made over a series of compounds shows, therefore, that the theoretical considerations which have been made are probably fundamentally true (see p. 134).

Methods for the Measurement of Transport Numbers.

Three methods are available for the measurement of transport numbers of ions in solution. The first, an analytical method, depends on the concentration changes which take place in the solution near each electrode during electrolysis. It was the method first used by Hittorf, and the technique of measuring these concentration changes has been improved considerably by Washburn. A second method which has been developed by Longworth and MacInnes makes use of the principle discovered by Lodge—

¹ T. Shedlovsky, *J. Amer. Chem. Soc.*, **54** (1932), 1411.

² MacInnes, Shedlovsky, and Longworth, *ibid.*, **54** (1932), 2758.

viz., that, due to the motion of the ions, the motion of a boundary between two solutions can be observed during the passage of a current and the mobility of the ion calculated. Finally, many careful measurements on the E.M.F.'s of the two types of concentration cells in which, respectively, transport does and does not occur, have been made to determine accurately the activity coefficients of the electrolytes used as the cell solutions. Provided these data are properly treated, they may be made to yield quite accurate values for the transport numbers of the ions present in the cells. We shall now discuss each of these principles in turn, and outline the experimental technique which has been adopted in order to obtain the best values for the transport numbers.

The Analytical Method.

The relation between the local changes in concentration near the electrodes, which take place on passing an electric current through an electrolyte, and the transport numbers of the two ions may easily be found. For if, in solution, the uni-univalent electrolyte (taking the simplest case)¹ is partially dissociated into free anions and cations, the concentration per unit volume of the anions c_- will be equal to the concentration per unit volume of the cations c_+ when there is no external electrical influence. The change in concentration at the anode when a current passes through the solution is due to the motion of the cations away from the liquid surrounding the anode. It will therefore be proportional to the concentration of cations in that neighbourhood and to their velocity under the applied potential gradient—i.e., it will be equal to kv_+c_+ . Similarly, the change in concentration at the cathode measured by the decrease in anion concentration will be kv_-c_- . Thus, the total fall in the concentration of the solution will be $kc_+(v_+ + v_-)$, since $c_+ = c_-$ and

$$\frac{\text{fall in concentration round the cathode}}{\text{fall in concentration round the anode}} = \frac{\text{cation speed}}{\text{anion speed}} \quad (94)$$

¹ For other valency types the argument is affected only in that different numbers of the two ions move towards the electrodes.

Now, this result is subject to one condition—viz., that there shall remain in the body of the solution a portion of the electrolyte which is unchanged in concentration throughout the process. For, if such a total change in concentration does take place, the volumes of the solution which are considered as being in the vicinity of the two electrodes will overlap and the changes in concentration which we have supposed to take place could not, in fact, be measured. From equation (86) it follows that

$$n_- = \frac{v_-}{v_- + v_+} = \frac{\text{fall in concentration around the anode}}{\text{total change in concentration of solution during electrolysis}} \quad (95)$$

and similarly for the anion transport number. The total change in concentration of the solution is usually measured

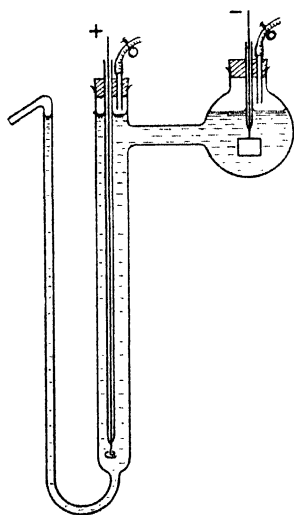


FIG. 39.—ANALYTICAL METHOD FOR MEASURING TRANSPORT NUMBERS (Nernst and Loeb).

by placing a coulometer, containing the same solution, in series with the transport apparatus. An analysis of this solution then gives the total change in concentration during electrolysis which is required in the above equation. In all the experimental arrangements of the analytical method it is to be noted that the quantities measured are the *total* anode and cathode concentration changes, and not the relative changes.

In the analytical methods, some difficulty has been found in preventing diffusion of the liquids during electrolysis. Hittorf used a porous membrane to prevent it, but such an arrangement interferes with the free motion of the ions. A better method makes use of the fact that during electrolysis the anode liquid tends to become denser, while the cathode liquid becomes lighter. The anode column is therefore made much longer than the cathode tube (see Fig. 39), and the anode liquid can then easily be

run out and analysed.¹ Furthermore, it may be demonstrated that no change in the concentration of the middle section of the electrolyte has taken place during electrolysis, by analysing the last portion of the solution run out from the anode column.

Unfortunately diffusion is not the only complicating factor which may interfere with the experimental accuracy of the Hittorf method. If solutions of considerable strength are electrolysed, convection currents are set up due to the heating effects of the electric current. Measurements of transport numbers made by this method are therefore confined to dilute solutions. In dilute solutions, however, if the current be passed through the solution for a long period of time, in order to get an appreciable change in concentration, the fast-moving hydrions and hydroxyl ions reach the central portion of the electrolyte and there change its composition. Hittorf attempted to minimise this effect by using a cadmium anode. Being easily oxidisable, cadmium dissolves, and so prevents the discharge of ions and the formation of a gas at the electrode. It is true that the Cd^{++} ions do migrate towards the cathode, but as their mobility is only about one-tenth that of the hydrogen ion, this effect is of no practical consequence. The use of a cadmium anode is, however, limited, since it prevents effectual stirring and it is better replaced by a mercury electrode covering a solution of the salt of some easily amalgamable metal like zinc. To prevent the formation of hydroxyl ions, Hittorf surrounded the cathode with a concentrated acid solution. But even when these precautions are taken, results of a high degree of accuracy cannot be obtained, for, on account of the concentration changes which take place in the electrode liquids, these tend to diffuse into one another.

In dilute solutions, if appreciable changes in concentration are to take place, either a very large quantity of solution must be electrolysed or the current must be passed for a very long time, during which there is more opportunity for diffusion to take place. By adopting the former alternative,

¹ Nernst and Loeb, *Z. physikal. Chem.*, 2 (1888), 948.

which is better for reducing diffusion errors, a very unwieldy apparatus would be required unless some modification were made in its design. Steele and Dennison,¹ however, reduced their apparatus to a normal size by flowing the middle portion of the liquid through the cell at intervals and testing the electrolyte removed for any change in concentration. In this way a large volume of liquid could be electrolysed, no matter how low the concentration. The formation of hydroxyl and hydrogen ions at the electrodes was prevented by a modified form of Noyes' device,² introducing known quantities of half normal acid and alkali into small cups surrounding the electrodes and allowing for the changes produced in concentration of the electrolyte. Steele and Dennison's measurements showed a variation of the transport number with concentration which, however, was attributed at that time, not to interionic attractions, but to complex ion formation.³

The best measurements which have been made by the analytical method adopt a somewhat different principle. When ions move under the influence of an applied potential gradient, they will carry with them solvent molecules, since they are solvated. If therefore a small quantity of some substance which is not affected by the solvent, and which is not an electrolyte, be added to the solution, any apparent changes in its concentration around the electrodes will be due to the motion of the solvent and hence of the carrier ions.⁴ The inert reference substance must be detectable with accuracy even at the low concentrations used, and mannite or raffinose is found to be particularly suitable.⁵

The use of an inert reference substance may, however, be dispensed with.⁶ The apparatus then consists essentially of a long tube of resistant glass (to reduce solution of alkali in the solution) which is of uniform bore throughout and

¹ Steele and Dennison, *J.C.S.*, **81** (1902), 456.

² Noyes, *Z. physikal. Chem.*, **36** (1901), 63.

³ Steele, *Phil. Trans. (A)*, **198** (1902), 105.

⁴ E. Buchböck, *Z. physikal. Chem.*, **55** (1904), 563.

⁵ E. B. Washburn, *J. Amer. Chem. Soc.*, **31** (1909), 322.

⁶ Jones and Dole, *ibid.*, **51** (1929), 1073.

Jones and Bradshaw, *ibid.*, **54** (1932), 130.

MacInnes and Dole, *ibid.*, **53** (1931), 1357.

which is bent several times at right angles, to reduce convection currents to a minimum. The tube is made in two parts connected by a ground-glass joint to facilitate accessibility to the middle portions (see Fig. 40). After electrolysis the solutions are divided up into five portions by means of the taps. These portions of the solution are called respectively the anode, anode middle (from anode side-tap to *a*), middle (from *a* to *c*), cathode middle, and cathode liquids. An analysis of these solutions may then be made accurately by a differential potentiometric method ¹ or by comparing the conductivities of the solutions with those of the original homogeneous solution. Such an arrangement has decided advantages over the Hittorf methods, since it reduces the diffusion of the electrode liquids, the local heating effects, and the inaccuracies in the analysis.

Moving Boundary Methods.

It must be realised that the inaccuracies inherent in the analytical methods, together with the impossibility of carrying out a sufficiently accurate analysis of the solution, do not render this principle really useful for investigating the concentration variations of transport numbers. Even with the improved apparatus of Washburn and Grinnell Jones which has been described, very few measurements have been carried out with sufficient accuracy for the results to be used to test the predictions of the interionic attraction theory. The few measurements which have been made have required very laborious experimental work. The ideal method for measuring transport numbers would be a direct method

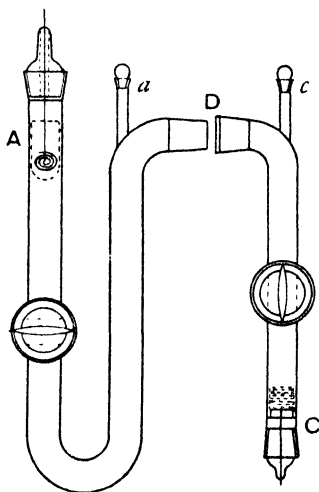


FIG. 40.—ANALYTICAL METHOD FOR TRANSPORT NUMBERS (Washburn).

¹ MacInnes and Dole, *J. Amer. Chem. Soc.*, **51** (1929), 1119.

in which the actual motion of the experimental ion was observed over any desired length of time. In this way the accuracy of the measurements could be increased without introducing any of the complicating factors involved in the analytical method when a dilute solution is electrolysed for a long period of time. Unfortunately it is never possible to determine directly the velocity of an ion. Any measurements of the movement of boundaries between two solutions under the influence of a potential gradient, do not give the velocity of the free ion, but the velocity of the ion constituent—i.e., of the ion in both the free and the combined state, which depends on the true degree of dissociation.¹

The principle of the moving-boundary method was first demonstrated experimentally by Lodge.² He showed that the hydrogen chloride formed from hydrogen ions which were produced during the electrolysis of a jelly containing sodium chloride, could be made to decolorise the red salt of phenolphthalein as the ions proceeded down the tube. Lodge's attempts to determine the velocities of other ions, by the formation of their precipitates with suitable reagents, were not, however, altogether satisfactory. The real difficulty in all moving-boundary methods is to form a boundary which is always reproducible. Whetham³ succeeded in showing that the use of jelly solutions or the formation of precipitates (provided these were only slight) did not interfere appreciably with the transport of the ions. When agar-agar is used to form jellies from the solutions, the constancy of the mobilities may be explained by the open, ring-like structure of the agar-agar molecule which allows the other relatively small ions to move freely through them while it has the effect of raising the viscosity of the solvent enormously.

As the formation of a precipitate is an irreversible process, measurements of the velocity of precipitate boundaries may be made only when the current is passing in one direction. If by the passage of one faraday, the observed boundary

¹ Miller, *Z. physikal. Chem.*, **69** (1909), 436.

² O. Lodge, *Brit. Assoc. Rep.* (1886).

³ W. C. D. Whetham, *Phil. Trans. (A)*, **186** (1895), 507.

moves through a volume V , then, provided the whole of the leading ion is replaced by the following ion,

$$n = VC \quad . \quad . \quad . \quad . \quad . \quad . \quad (96)$$

where C is the concentration of the solution of the ion and n is the transport number with respect to the sides of the tube, and not with respect to the solution. For the passage of a smaller quantity of current—say, f coulombs—resulting from the passage of a steady current i ampères for t seconds, a smaller volume v is swept out by the boundary, which is related to V by the expression :

$$\frac{v}{V} = \frac{f}{F} \quad . \quad . \quad . \quad . \quad . \quad . \quad (97)$$

Substituting therefore for V in (96), we have :

$$n = \frac{vCF}{f} \quad . \quad . \quad . \quad . \quad . \quad . \quad (98)$$

or
$$n = \frac{vCF}{it} \quad . \quad . \quad . \quad . \quad . \quad . \quad (99)$$

Whetham's method is, however, not generally applicable, for there are only a few pairs of solutions which fulfil the required conditions for the formation of a good boundary. Moreover, corrections must be made for the shrinkage of the vertical column of the liquid when its concentration changes in the neighbourhood of the electrodes.

If a double boundary is used, such as may be formed, for example, by stratifying the salt between solutions having the same anion and cation respectively, and the one being lighter and the other heavier than the observed solution, a direct measurement of the current may be avoided. For if n_+ and n_- represent the transport numbers of the two ions for the observed solution,

$$\left. \begin{aligned} n_+ &= \frac{v_+ FC}{it} \\ n_- &= \frac{v_- FC}{it} \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (100)$$

and

and since from (87) $n_+ + n_- = 1$

we have
$$n_+ = \frac{v_+}{v_+ + v_-} \quad . \quad . \quad . \quad . \quad (101)$$

Steele has applied this double boundary method in a modified form to give quite accurate results. A direct comparison of the velocities of the anion and of the cation is made in two vertical tubes of equal cross section enabling the ratio v_+/v_- to be determined directly. The principle may be extended to cases where stable gelatine jellies are not formed, by observing the boundaries between two stratified colourless solutions by their difference in refractive indices.

It is obviously a matter of great importance in the moving-boundary method, that a clear boundary which always has the same velocity at every point should be maintained. For this, the "indicator" or following ion which, together with the measured ion, forms the boundary, must conform to a number of conditions, on the observance of which the accuracy of the method largely depends. These conditions may be summarised as follows, that :

(1) the indicator ions should have specific velocities less than those of the ions to be measured. This condition was first emphasised by Whotham ;

(2) the indicator should not react chemically with the solutions being examined ;

(3) no ions should be produced in the cell which would overtake the boundary,

(4) the lighter solutions should lie over the heavier ;

(5) the indicator should have a resistance not very much greater than that of the solution it follows in order to avoid disturbance of the boundaries by the heating effects of the current ;

(6) the potential fall should lie between particular limits depending upon the nature of the solutions forming the boundary. This condition is found to be of great importance ;

(7) the solutions forming the two sides of the boundary must have a common ion.

When these conditions were carefully observed, it was found that very accurate measurements were possible with a minimum of trouble. This seemed to show that improvements in this technique would be more likely to give accurate

results in very dilute solutions than the analytical methods. In Steele's measurements the difficulties of the visual method were multiplied, in some respects at least for, while it was quite possible to obtain one good boundary for a particular substance, it was a much more difficult matter to obtain two simultaneously. All recent measurements of transport numbers adopting the moving-boundary principle therefore use only one boundary which requires only one reversible electrode for its formation. Since the transport number which is measured is that of the leading ion, great care must always be exercised in the choice of a suitable indicator ion. For most purposes lithium, which is lighter and slower than almost every other positive ion, is very suitable for boundaries moving downwards, while the cadmium ion is a good indicator for boundaries moving upwards.

When the boundaries are to be formed without using jellies, considerable difficulties are experienced in minimising the effects of diffusion. Obviously it is impossible to do this simply by floating the lighter on the heavier solution. Two methods have therefore been employed in general for the formation of the boundaries. The first of these, by which "autogenic" boundaries are said to be formed,¹ depends on the formation of the indicator solution from its metal, in the first solution. For example, if the top or bottom of the vessel containing the solution is composed of the indicator metal and a current is passed from the metal into the solution, the metal will dissolve and the boundary required will proceed along the tube.

As this method of forming the boundary is restricted in its application, a more general method has been introduced² which employs the ingenious device of cutting off the end portions of two solutions and sliding the cut faces on to one another. The apparatus (Fig. 41) consists of two sections which would be formed if the entire apparatus were cut

¹ MacInnes and Longworth, *Chem. Rev.*, **11** (1931), 170.

² MacInnes and Brighton, *J. Amer. Chem. Soc.*, **47** (1925), 994.
Longworth, *ibid.*, **54** (1932), 2741; **57** (1935), 1185.

MacInnes and A. S. Brown, *ibid.*, **57** (1935), 1356; *Chem. Rev.*, **18** (1936), 335, have also used this method for establishing the liquid junction between two solutions of the same electrolyte in concentration cells (see Chapter IX).

through the tube in which the boundary is to be observed. Each of these portions has an electrode, silver for the cathode and silver-silver chloride for the anode, surrounded by a buffer tube *T* which prevents changes of the concentration of the electrolyte in the vicinity of the electrodes from affecting the solutions in the observation tube. The

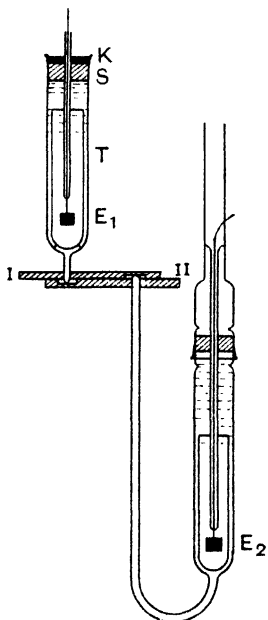


FIG. 41.—LONGSWORTH'S METHOD FOR MEASURING TRANSPORT NUMBERS.

importance of this condition was realised¹ long before the recent types of moving-boundary apparatus had been designed, and it is noticeable that in Dennison and Steele's measurements, the correction for this error becomes greater, the higher the concentration. The two parts of the observation tube which we have supposed cut in two each terminate in well-lubricated glass plates which have their opposite accurately planed faces, *A* and *B*, in contact. When the two parts of the apparatus are filled and the electrodes are in position, a drop of each solution protrudes from the observation tubes into a hole in the opposite plate. The whole apparatus is then immersed in a thermostatic vessel and, as soon as temperature equilibrium is restored, a spring is released which causes the two glass plates to rotate slowly,

first cutting off the columns of the two solutions sharply and then bringing one over the other so that the boundary is established.

One of the most important of the other conditions which must be observed if accurate results are to be obtained is the maintenance of a constant current through the apparatus. As the boundary progresses, one electrolyte is replaced by another and the resistance of the electrolyte gradually

¹ G. N. Lewis, *J. Amer. Chem. Soc.*, **32** (1910), 862.

changes. For the maintenance of a constant current, therefore, the potential across the electrolyte must be continuously varied so as to keep the current at a constant value.¹

Effects on the boundary, such as may arise from vibration of the apparatus, are found to have an appreciable influence only on the "thickness" or sharpness of the boundary, and not on its velocity. It has been suggested that the large space charge which must be present at the boundary will affect its motion appreciably.² But the close agreement between the best results from the analytical method and from the moving-boundary measurements (see below) show that this space charge cannot appreciably affect the accuracy of the visual method.³ Another factor which might at first appear to be more important is the volume correction. If ΔV represents the difference between the observed volume swept out by the boundary and the volume V with respect to the water, Lewis has shown⁴ that

$$n = VC = (V_{\text{obs.}} - \Delta V)C = n_{\text{obs.}} - C\Delta V \quad . \quad (102)$$

This volume correction, however, can be made only approximately, but as the correction is in any case small, the error which may be introduced in making it is quite negligible. When the necessary corrections have been made for the conductivity of the solvent (which is as important in transport-number measurements of very dilute solutions as it is in conductivity measurements) and for the volume correction, results by the moving-boundary method may be obtained, which are reproducible to within 0.02%.⁵ Moreover, the results agree remarkably well with the best measurements made analytically, although there are only a few ions for which data of sufficient accuracy are available to make comparison possible. In Table III, showing these results, the values obtained by the analytical method for

¹ Longworth and MacInnes, *J. Opt. Soc. Amer.*, **19**, (1929), 50.
MacInnes, Cowperthwaite, and Blanchard, *J. Amer. Chem. Soc.*, **48** (1926), 1909.

² "Physical Chemistry," ed. H. S. Taylor, New York (1931), p. 685.

³ MacInnes and Dole, *J. Amer. Chem. Soc.*, **53** (1931), 1357.

⁴ G. N. Lewis, *ibid.*, **32** (1910), 862.

⁵ Longworth, *ibid.*, **56** (1932), 2761.

the transport numbers of K^+ in potassium chloride and of Li^+ in lithium chloride have been extrapolated by means of an empirical equation, so that too much confidence

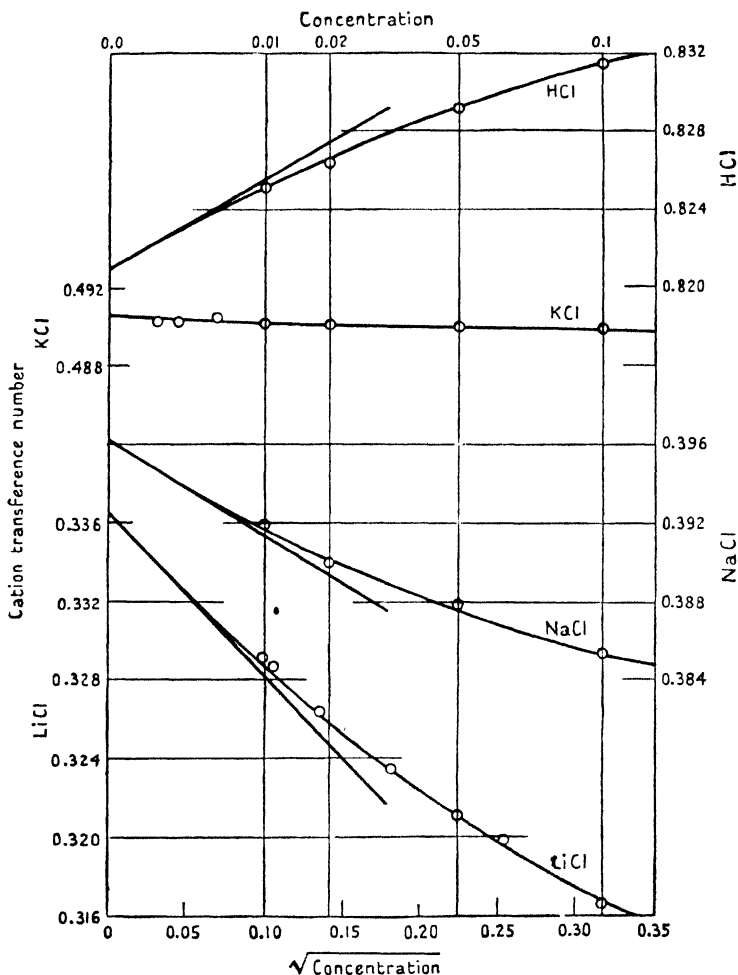


FIG. 42.—TRANSPORT NUMBERS AS A FUNCTION OF THE CONCENTRATION.

cannot be placed in them. A comparison of the observed transport numbers, determined at different concentrations within the limiting range, with the limiting slopes given by

TABLE III

*Transport Numbers of some Ions*¹

Concentration.	Transport numbers of K ⁺ in KCl at 25°.		Transport numbers of Li ⁺ in LiCl at 25°.			Transport numbers of Ba ⁺⁺ in BaCl ₂ at 25° C.	
	Moving-boundary method. ²	Analytical method. ³	Moving-boundary method. ⁴	Analytical method (interpolated). ⁵	From E.M.F. measurements (interpolated). ⁶	Analytical method. ⁷	From E.M.F. measurements (interpolated). ⁸
0.01	0.4898	—	0.3289	0.3289	0.3333	0.4378	0.4348
0.02	0.4896	0.4893	0.3261	0.3269	—	—	—
0.05	0.4900	0.4894	0.3211	0.3230	0.3258	0.4253	0.4223
0.10	0.4899	0.4898	0.3168	0.3187	0.3203	0.4162	0.4131
0.50	0.4887	0.4896	—	0.3006	0.2975	0.3792	0.3766
1.0	0.4883	0.4875	—	0.2897	0.2812	0.3528	0.3488

¹ The values of the limiting transport numbers are not given, since the equations used for interpolating the results in columns 5, 6, and 8 are not accurate at very low concentrations, and the limiting values so obtained for the transport numbers would not give an unequivocal comparison with those by the other experimental methods.

² Longworth, *J. Amer. Chem. Soc.*, **54** (1932), 2755.

³ MacInnes and Dole, *ibid.*, **53** (1931), 1358.

⁴ Longworth, *loc. cit.*

⁵ Jones and Bradshaw, *J. Amer. Chem. Soc.*, **54** (1932), 138.

⁶ Jones and Bradshaw, *loc. cit.*

⁷ Jones and Dole, *J. Amer. Chem. Soc.*, **51** (1929), 1073.

⁸ Jones and Dole, *loc. cit.*

equation (92) show very good agreement for uni-univalent salts (see Fig. 42).⁹ For salts of other valency types, however, the experimental curve does not correspond with the limiting straight line of the Onsager theory, although the sign of $\frac{\partial n}{\partial \sqrt{c}}$ has always been found to be that predicted by equation (92).¹⁰ The range of application of the Onsager theory to transport numbers in unsymmetrically valent

⁹ Lucasse, *J. Amer. Chem. Soc.*, **47** (1925), 1743.

Longworth, *ibid.*, **57** (1935), 1185.

Jones and Prendergast, *ibid.*, **58** (1936), 1476.

G. S. Hartley and Donaldson, *Trans. Faraday Soc.*, **33** (1937), 457.

¹⁰ In Fig. 42 the circles represent the experimentally observed points; the full curve is plotted from the extended equation

$$n_+ = (n_+)_{\infty} - \frac{[1 - 2(n_+)_{\infty}]\beta\sqrt{c}}{A_{\infty} - (\alpha A_{\infty} + 2\beta)\sqrt{c}} + \frac{\beta\sqrt{c}}{A_{\infty} - (\alpha A_{\infty} + 2\beta)\sqrt{c}} \quad (103)$$

which is obtained in the same way as Shedlovsky's equation (91) for the conductivity at low concentrations. The straight lines have the slope given by the limiting equation (92).

electrolytes therefore agrees with the range of its application to ordinary conductivity measurements.

An interesting extension of the use of Longworth's moving-boundary method has been the investigation of the transport numbers of potassium chloride, hydrogen chloride, and deuterium chloride in mixtures of light and heavy water.¹ Measurements of the properties of electrolytes in mixtures of light and heavy water are of particular interest, since it is possible to obtain a uniform variation in the physical properties of the solvent without introducing any secondary effects due to interaction between the two molecular species present in the mixture. The transport-number measurements have shown wide variations of the transport numbers of the cations in the chlorides with the molar fraction of heavy water present. These wide variations of the transport numbers with a change in properties, particularly of the viscosity of the solvent, are not at all in agreement with Walden's rule (equation 520) according to which

$$\Lambda_{\infty} \eta = \text{constant}$$

where η is the viscosity of the solvent. For, considering a binary electrolyte, Walden's rule gives that :

$$\begin{aligned} (\lambda_+)_{\infty} \eta &= k_+ \\ (\lambda_-)_{\infty} \eta &= k_- \\ \text{i.e., } (n_+)_{\infty} &= \frac{(\lambda_+)_{\infty}}{(\lambda_+)_{\infty} + (\lambda_-)_{\infty}} = \frac{k_+}{k_+ + k_-} \quad (104) \end{aligned}$$

and the limiting cation transport number should be independent of the solvent. These deviations from Walden's rule are interesting in view of other cases where the rule fails to describe the observed behaviour (see Chapter XI).

Determinations of Transport Numbers from E.M.F. Measurements.

The third principal method for estimating transport numbers depends on the fact that there are two types of reversible concentration cells each type having a different

¹ L. G. Longworth and D. A. MacInnes, *J. Amer. Chem. Soc.*, 59 (1937), 1666.

E.M.F.¹ In the first of these, the two electrode liquids are connected through a liquid junction in such a way that transport of the common ion may take place. The E.M.F. of such an arrangement is given by equation (435) as

$$E = - \frac{2RT}{zF} n \ln \left(\frac{a_1}{a_2} \right) \quad . \quad . \quad . \quad (435)$$

in which a_1 and a_2 are the mean ion activities at the two concentrations c_1 and c_2 and n is the mean transport number over this range (see p. 287). Since, however, the transport number changes over the concentration range c_1 to c_2 , the E.M.F. is strictly the integral from one solution to the other, of equation (436), viz. :

$$E = \int_1^{II} dE = - \frac{2RT}{zF} \int_1^{II} n d \ln a = - \frac{2RT}{zF} \int_1^{II} n (d \ln c + d \ln f)$$

Now, an accurate integration of this is possible only if both n and a (or f , the activity coefficient) are known accurately as functions of the concentration.

MacInnes and Beattie,² who first attempted to make accurate measurements of the transport number of the lithium ion by this method, employed a complicated and somewhat arbitrary method of interpolation in equation (436), by fixing a concentration to which all measurements of the concentration cells might be referred. The variation of the E.M.F. with the logarithm of the activity then showed a decided curvature due to the change of transport number with concentration (see Fig. 43). If, however, the liquid junction through which transport can take place is avoided in constructing

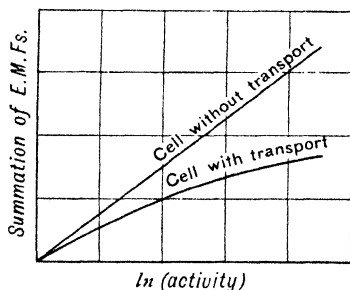


FIG. 43.—ESTIMATION OF TRANSPORT NUMBERS FROM E.M.F. MEASUREMENTS.

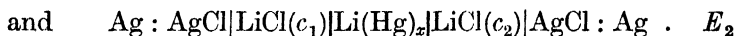
¹ A "concentration cell" is a cell in which the E.M.F. depends on a difference of concentration between two solutions of an electrolyte each in contact with a similar reversible electrode.

² MacInnes and Beattie, *J. Amer. Chem. Soc.*, **42** (1920), 1117.

the cell, by using metal amalgam electrodes and by using an apparatus where no oxidation of the amalgams can take place, the E.M.F. expression does not involve the transport number and is [equation (378)]

$$E_2 = - \frac{2RT}{zF} \ln \frac{a_1}{a_2}$$

If therefore the E.M.F.'s of two cells of the types



be plotted against the logarithms of the mean activities, the ratio of the E.M.F.'s for any value of $\ln a$ will give a value for the relevant transport number at the corresponding concentration, using only E.M.F. measurements.

Unfortunately MacInnes and Beattie's arbitrary method for interpolating the values for the E.M.F.'s of cells with transport does not give the correct variation of the transport number with concentration.¹ The development in the theory of interionic attraction has, however, led to expressions for the variations of the activities and transport numbers of ions as functions of the concentration. Thus the Hückel equation (320):²

$$\ln f = - \frac{0.354\sqrt{2c}}{1 + A\sqrt{c}} + Bc$$

has been shown to represent the variation of the activity coefficient with concentration up to quite high concentrations. The empirical equation of Shedlovsky for the conductivity (equation 59) which has been found to hold for uni-univalent electrolytes up to 0.1N gives, for the variation of the transport number with concentration, the expression

$$n_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-} = \frac{(\lambda_+)_{\infty} + [\alpha(\lambda_+)_{\infty} + \beta]\sqrt{c} + B'c[1 - \alpha\sqrt{c}]}{A_{\infty} - (\alpha A_{\infty} + \beta)\sqrt{c} + Bc(1 - \alpha\sqrt{c})} \quad (105)$$

¹ Jones and Bradshaw, *J. Amer. Chem. Soc.*, **54** (1932), 138.

² Hückel, *Physikal. Z.*, **26** (1925), 93.

Unfortunately the equation for the E.M.F. of a cell with transport between the concentrations c and $c + dc$, in which these accurate equations for the variations of n and α are substituted, has not yet been integrated. The accuracy with which measurements of the E.M.F.'s have been obtained make it certain, however, that if the results can be correctly interpreted, the method should give the most accurate values for the transport numbers of all the methods available for determining them. A certain number of measurements have been made by substituting the Hückel equation into the equation for the E.M.F. of a cell with transport, and estimating the constants empirically from the available data.¹ The values obtained for the transport numbers may be expressed by the equation

$$n = \frac{k_1}{1 + k_2\sqrt{c}} - 1 \quad . \quad . \quad . \quad (106)$$

which, although not extrapolating correctly to very dilute solutions, is obeyed with fair accuracy in the middle concentration range. The values calculated for the transport numbers in this range are in quite good agreement with the best values by the unequivocal moving-boundary method (see Table III, p. 129). A criticism which might be raised against the use of E.M.F. measurements for determining transport numbers unequivocally is apparent from a consideration of the method used for measuring the E.M.F.'s of cells with transport. It is necessary in these experiments to allow for the liquid junction potential, and since the passage of a current through a cell, when this involves transport across the intermediate diffusion layer, is an irreversible process, it is not possible to represent the E.M.F. by an equation deduced only from thermodynamic considerations.² The error introduced in the cases already investigated by the E.M.F. method, cannot, however, be very great, since the results show good agreement with the values by direct measurement.

¹ Jones and Dole, *J. Amer. Chem. Soc.*, **51** (1929), 1073.

² J. J. Hermans and L. J. Oosterhoff, *Phil. Mag.*, **24** (vii) (1937), 304.

Limiting Individual Ion Conductances.

Now, from the values for the limiting transport numbers obtained by extrapolating the experimental results with equation (91), together with the limiting equivalent conductivities of salts, which have been obtained by Shedlovsky,¹ it is possible, from equation (93),

$$\lambda_{\infty} = \Lambda_{\infty} n_{\infty}$$

to obtain values for the limiting individual ion conductivities.² Moreover, the data for a set of salts having the same anion (e.g., the chlorides of potassium, sodium,

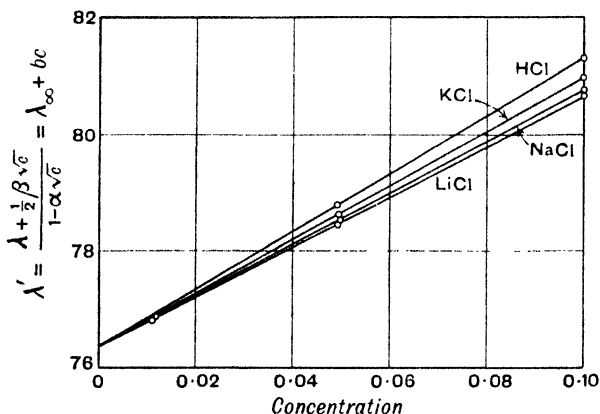


FIG. 44.—ION CONDUCTANCES OF CHLORIDE ION.

lithium, and hydrogen) each give independent values for the limiting conductance of the anion. In this way exactly the same value of λ_{∞} for the chloride ion has been obtained from four quite different sets of data (see Fig. 44). This is in itself an excellent confirmation of the extreme accuracy of the moving-boundary method and of the Shedlovsky method for determining the conductivities of very dilute solutions. Values for the limiting ion conductivities have also been obtained by extrapolating the values of λ found from the relation

$$\lambda = \Lambda n \quad . \quad . \quad . \quad . \quad . \quad (107)$$

¹ Shedlovsky, *J. Amer. Chem. Soc.*, **54** (1932), 1411.

² MacInnes, Shedlovsky, and Longworth, *ibid.*, **54** (1932), 2758.

by means of the Shedlovsky equation (60) :

$$\lambda_{\infty} = \frac{\lambda + \beta\sqrt{c}}{1 - \alpha\sqrt{c}} - Bc = \lambda'_{\infty} - Bc$$

Results obtained by this method of extrapolation agree very well with those from the extrapolated transport number and conductivity measurements. The fact that all the results obtained experimentally for the transport numbers and for the limiting ion conductivities form such a mutually supporting and confirming body of evidence, is an excellent confirmation of the applicability of the interionic theory, and of Onsager's treatment of this for non-stationary processes, to very dilute solutions of strong electrolytes.

CHAPTER V

THE VISCOSITIES, DIFFUSIONS, COMPRESSIBILITIES AND SURFACE TENSIONS OF STRONG ELECTROLYTES

IN the last chapter we used the theory of interionic attraction for considering the irreversible process of the conduction of electricity in an electrolyte—*i.e.*, the constrained motion of the ions through the solution under the influence of an applied electric field. But conductivity is only a special case of the general migration of ions in a solution, and it is not strictly logical to give it a preferential treatment. The only reason indeed, for dealing with the problem at such length is because far more experimental work has been carried out on this property than on any of any other irreversible properties. Diffusion, where the ions move freely, and viscosity, where they move under a shearing force, must both be considered as irreversible processes. Onsager and Fuoss have therefore worked out, by the aid of special mathematical methods, the general solution for the effect of interionic attraction on any irreversible process in an electrolyte or in a mixture of electrolytes.¹ They find that, no matter how many types of ions may be present in solution, provided the *total concentration* c of all the ionic species together is low, the value of the irreversible function $F(c)$ at a concentration c will be related to the value of the function at infinite dilution $F(o)$ by the equation

$$F(c) = F(o) + \alpha\sqrt{c} \quad . \quad . \quad . \quad (108)$$

More exact computations have been made to extend this relation to higher total concentrations, and although this problem has not been completely solved, the calculations lead to an expression of the form

$$F(c) = F(o) + \alpha\sqrt{c} + \beta c \log c + \gamma c + . \quad . \quad . \quad (109)$$

¹ Onsager and Fuoss, *J. Phys. Chem.*, **36** (1932), 2689.

Special Case of Viscosity.

If we consider the special case of the viscosity of a strong electrolyte solution, the applied force is here a shearing force distributed over parallel planes of the liquid along the direction of application of the force. The liquid will therefore have different velocities at different planes, and in the special case of perfect viscous flow there will be a uniform velocity gradient at right angles to the applied force. Falkenhagen first pointed out that, as a consequence of this velocity gradient, the atmosphere round an ion which is assumed to be spherically symmetrical when it is at rest, will be distorted into an ellipsoid (Fig. 45). There will therefore be a force on the ions due to this distortion in addition to the original shearing force.¹

It is obvious that the degree of asymmetry of the ion atmosphere when the ion is in motion depends on the magnitude of the velocity gradient. The displacement of electric charges takes place progressively along the direction of the velocity gradient, and since it results from the additional shearing force it is therefore proportional to the displacement—*i.e.*, to the velocity gradient. We may therefore expect a positive viscosity effect in electrolyte solutions due to the presence of an ion atmosphere around each ion.

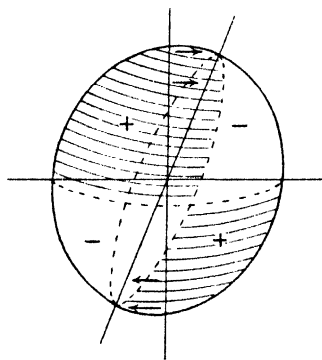


FIG. 45.—ION ATMOSPHERE DISTORTED BY A SHEAR FORCE.

A complete solution of the problem would therefore require a knowledge of the exact distributions of ions of the type j in the atmosphere due to an ion of the type i . The electric densities—*i.e.*, the functions representing the distributions of charge in different parts of the ion atmosphere—may then be found in terms of these distribution functions, and the shearing forces involved in the distortion of the symmetrical configurations may be calculated.

¹ Falkenhagen and Dole, *Physikal. Z.*, **30** (1929), 611.
Falkenhagen, *Nature*, **127** (1931), 439.

A simple calculation suffices, however, to illustrate the nature of the effect.¹ We will suppose the electrolyte solution to be confined between parallel plates h cm. apart, the lower one fixed and the upper moving with a constant velocity v in the positive direction of x (Fig. 46). Assuming

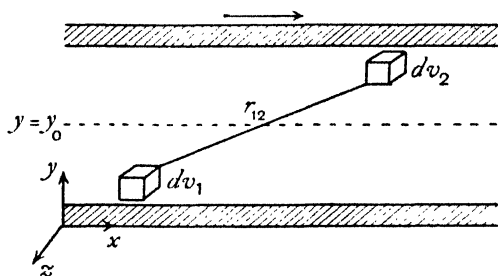


FIG. 46.—VISCIOUS FORCES IN AN ELECTROLYTE.

now a constant velocity gradient in the y direction, this will be given by

$$\frac{\partial v_x}{\partial y} = \frac{v_1}{h} \quad . \quad . \quad . \quad . \quad (110)$$

then the velocity at the level y is

$$v_x = (v_1/h)y \quad (v_y = 0; v_z = 0)$$

From the definition of viscosity, a stress

$$S_{xy} = \eta \frac{\partial v_x}{\partial y} \quad . \quad . \quad . \quad . \quad (111)$$

per unit area is transferred from each layer of liquid to the next beneath it. Considering now the distorted ion atmosphere, the electrostatic forces and the thermal agitation which tend to restore the disturbed atmosphere to its initial symmetrical configuration require a definite time of relaxation τ in which to operate. If, in the present case, the relative rate of deformation is $\frac{\partial v_x}{\partial y}$, then a stationary deformation $\tau \frac{\partial v_x}{\partial y}$ will persist. Thus the deformation of the ion atmosphere due to viscous forces will be of the order

¹ It is important to note that the following analysis is not rigid, and it can give no information about the magnitude of the constants involved in the final equation for the viscosity of the solution.

$$\frac{\rho}{\kappa^2 kT} \cdot \frac{\partial v_x}{\partial y} \quad . \quad . \quad . \quad . \quad . \quad (112)$$

where we have substituted for τ from equation (17).

Now, two ions of charge e situated at a distance $1/\kappa$ apart will serve to represent formally the central ion and its ion atmosphere. They will exert on one another a Coulomb force $\frac{e^2 \kappa^2}{D}$, so that the total transport force between an ion and its atmosphere without regard to direction is

$$\frac{1}{\kappa} \cdot \frac{e^2 \kappa^2}{D} = \frac{e^2 \kappa}{D} \quad . \quad . \quad . \quad . \quad (113)$$

The resultant directed fraction of the total stress caused by deformation may be supposed to be of the same magnitude as (112), so that the stress S_{yx} transferred between an ion and its atmosphere is of the order

$$\frac{e^2 \kappa}{D} \cdot \frac{\rho}{\kappa^2 kT} \cdot \frac{\partial v_x}{\partial y} \quad . \quad . \quad . \quad . \quad (114)$$

or for n ions, taken in pairs,

$$\frac{ne^2 \rho}{\kappa D kT} \cdot \frac{\partial v_x}{\partial y} \quad . \quad . \quad . \quad . \quad (115)$$

Making the transformation (equation 262)

$$\kappa = \sqrt{\frac{8\pi ne^2}{DkT}}$$

in this expression, we have :

$$S_{yx}^* \approx k\rho \frac{\partial v_x}{\partial y} \quad . \quad . \quad . \quad . \quad (116)$$

giving the added stress transferred in addition to that due to friction between the solvent molecules. The latter is, of course,

$$S_{xy}^0 = \eta_0 \frac{dv_x}{dy} \quad . \quad . \quad . \quad . \quad (117)$$

where η_0 is the viscosity of the pure solvent. The electrostatic forces therefore cause an addition to the viscosity of the pure solvent, of magnitude

$$\eta^* \approx \kappa \rho = A^* \kappa \rho \quad . \quad . \quad . \quad . \quad (118)$$

which, since it contains κ is proportional to $\sqrt{c}$. Hence

$$\eta = \eta_0 + A^1\sqrt{c} \quad . \quad . \quad . \quad (119)$$

or
$$\frac{\eta}{\eta_0} = \phi = 1 + A\sqrt{c} \quad . \quad . \quad . \quad (120)$$

where A is now a function of the viscosity of the pure solvent, the temperature and the valencies and mobilities of the ions, and ϕ is the relative viscosity.

From this equation we may calculate the order of the viscosity effect for a typical uni-univalent electrolyte in sufficiently high dilutions. The more complete analysis gives the exact value of the constant A_1 and for a solution of potassium chloride at 25° C. the substitution of the values of the various constants gives :

$$\eta^* = 44.7 \times 10^{-6}\sqrt{c} = 5.0 \times 10^{-3}\eta_0\sqrt{c} \quad . \quad (121)$$

For an N/10 solution of this electrolyte *assuming that the Debye-Falkenhagen analysis could be applied to such a high concentration*, the positive viscosity effect would amount to only 0.14% of η_0 —i.e., the predicted value of ϕ would be 1.0014. Over ranges of concentration where the theory could be applied, the effect would probably be far less, and the measurements would have to be undertaken with a very high degree of accuracy if they were to be of value in testing the applicability of the Debye theory to the viscosity effect. Accurate determinations of the viscosities of strong electrolytes were first made by Jones and Dole¹ on barium chloride solutions, but the majority of their measurements were carried out at concentrations too high to be of real use in confirming the theoretical equation. Their results could be expressed empirically by the equation

$$\phi = 1 + A\sqrt{c} + Bc \quad . \quad . \quad . \quad (122)$$

but although the A values are in fair agreement with those calculated from the theory in equation (120), the constant B appears to have no theoretical significance.² These experiments only showed a positive viscosity effect [$\phi > 1$]

¹ Grinnell Jones and Dole, *J. Amer. Chem. Soc.*, **51** (1929), 2980.

² Lawrence and Wolfenden, *J.C.S.* (1934), 1144.

in the region of quite dilute solutions. The decrease in viscosity which has been observed at higher concentrations may be due to depolymerisation of the solvent molecules by the ions. This suggestion was, in fact, made to account for the observed values of ϕ long before the theoretical explanation of the viscosity effect was put forward.

Experimental Determinations of Relative Viscosity.

The most convincing verification of the limiting law for the concentration variation of viscosity is provided by the work of Wolfenden and his collaborators.¹ The theory of Falkenhagen is valid for aqueous solutions at concentrations not exceeding 0.01N, where the maximum relative viscosity is 1.001. Measurements must therefore be made to an accuracy of at least 1 part in 10,000. The exact form of the viscometer has been shown to determine in part the values obtained for the viscosity, since the magnitude of the deviations from Poiseuille's law which the results show, depends on the design of the instrument. Further difficulties may arise unless the viscometer is constructed of resistant glass, otherwise it is found that each quantity of pure water and solution run through the capillary increases the diameter by its solvent action so that the water constant requires frequent re-determination.

In the best experimental arrangements a differential determination of the viscosity of the solvent and the solution is made in two similar viscometers arranged side by side in the same thermostat. In this way many errors due to variations of temperature and pressure are minimised. The experimental evidence shows that, although the Falkenhagen theory gives the experimentally determined values of A over a very small range of high dilutions, and therefore predicts the correct limiting slopes (of the curve viscosity $\sqrt{\text{concentration}}$) for uni-univalent electrolytes, the behaviour of electrolytes of more complicated valency types—e.g., LaCl_3 and MgSO_4 —is not explained by the

¹ W. E. Joy and Wolfenden, *Proc. Roy. Soc., A*, **134** (1931), 413.

W. H. Cox and Wolfenden, *ibid.*, **A**, **145** (1934), 475.

Also Grinnell Jones and Talley, *J. Amer. Chem. Soc.*, **55** (1933), 624.

E. Asmus, *Z. Physik.*, **108** (1938), 491.

simple theory (see Fig. 47). This agrees with the results obtained for other properties of electrolytes of complicated valency types. The few measurements which have been made on the viscosities of non-aqueous solutions show that, as for the conductivities of these solutions, the experimental results are only in qualitative agreement with the simple theory. It is possible that in these cases other ionic species

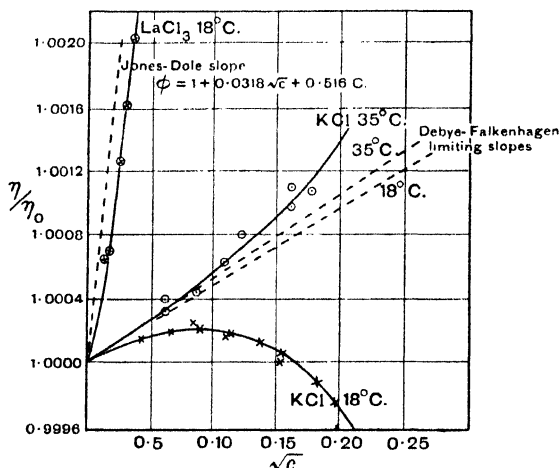


FIG. 47.—VISCOSITIES AS A FUNCTION OF CONCENTRATION FOR SOME ELECTROLYTES.

are appearing in the solution which should be taken into account in considering any of their properties.¹

Diffusion in Strong Electrolytes.

There is even less experimental evidence available for diffusion in solutions of electrolytes, than for the viscosities. The diffusion constant $\mathfrak{D}$, which measures the tendency of the ions to move under external forces, is most familiar to us from Fick's law. This states that, for unidirectional diffusion, along a line parallel to the x axis,

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(\mathfrak{D} \frac{\partial c}{\partial x} \right) \quad . \quad . \quad . \quad . \quad (123)$$

where c is the concentration and t the time. Since $\mathfrak{D}$ is

¹ R. Zuber and K. Sitte, *Z. Physik*, **79** (1932), 306.

itself a function of the concentration, its value at any given concentration will be the "differential" diffusion coefficient. Onsager and Fuoss were able to compute the dependence of η upon c from their general analysis of irreversible processes. They equated η to the product of two terms, one representing the change in thermodynamic potential of the solute with concentration, the other a "mobility" term

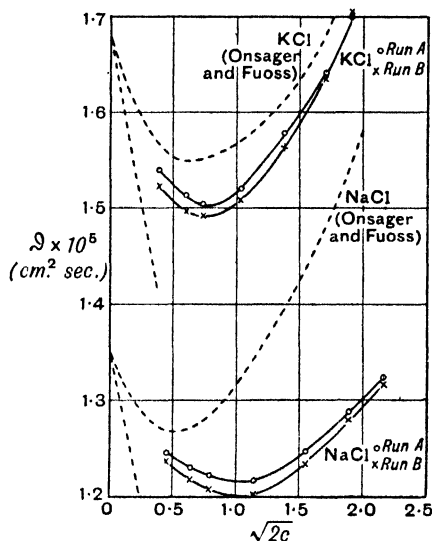


FIG. 48.—DIFFUSION COEFFICIENTS OF ELECTROLYTES.

which was calculated from the Debye-Onsager theory. For a binary electrolyte their equation reduced at 18° to

$$\eta = 4.842 \times 10^{10} \left(\frac{\bar{\Omega}}{c} \right) \cdot \left(1 + c \frac{\partial}{\partial c} \ln f_{\pm} \right)$$

where $\bar{\Omega}$ is a complicated function of the ion conductances and the concentration. This equation predicts that there should be a minimum value for η at some concentration in the range 0.1–1.0N. But although it does predict the correct shape of the curves for η against $\sqrt{c}$ (see Fig. 48), the equation is not altogether satisfactory. The only experimental results which are available are for uni-univalent electrolytes. The best of these have been obtained by an

interferometric method¹ and by a diaphragm cell method,² but data for the diffusion coefficients at very low concentrations are not available. It is safe, however, to assume that any theory of the diffusion of electrolyte solutions which is not completely satisfactory for uni-univalent salts will be still less applicable to salts of other valency types. Recently a semi-empirical equation has been proposed³ which predicts the differential diffusion constants of the three uni-univalent salts which have been examined, within the limits of experimental error up to concentrations of about normal. These salts are potassium chloride, sodium chloride, and potassium nitrate, and only their aqueous solutions have been studied.

Compressibilities of Strong Electrolytes.

Two other effects in electrolytes will now be considered—viz., the compressibilities and surface tensions of their solutions—which, although they are thermodynamic, not irreversible processes, are best dealt with here. The apparent molecular compressibility is defined as the difference between the compressibility of a solution containing one mole of the solute and that of the pure solvent—i.e., as

$$\phi(K_2) = \beta V - \beta_1 V_1 \quad . \quad . \quad . \quad (124)$$

$$\left. \begin{array}{l} \text{where} \\ \text{and} \end{array} \right\} \begin{array}{l} \beta = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T \\ \beta_1 = -\frac{1}{v_1} \left(\frac{\partial v_1}{\partial P} \right)_T \end{array} \quad . \quad . \quad . \quad (125)$$

are the coefficients of compressibility for the solution and for water respectively, and V and V_1 are the corresponding molar volumes. All the experimental evidence which is available goes to show that this apparent molar compressibility is proportional to the square root of the concentration⁴ over quite wide concentration ranges and not merely over a small range of very low concentrations. For the same errors in β the uncertainty in the values of the partial molar

¹ Clack, *Proc. Physical Soc.*, **36** (1924), 313.

² McBain and Dawson, *Proc. Roy. Soc., A*, **148** (1935), 32.

³ A. R. Gordon, *J. Chem. Phys.*, **5** (1937), 522.

⁴ B. J. Moir and E. N. Lauman, *J. Amer. Chem. Soc.*, **56** (1934), 300.
Gucker, *ibid.*, **55** (1933), 2709.
Falkenhagen, *Z. Electrochem.*, **41** (1935), 570.
A. Szaley, *Physikal. Z.*, **35** (1934), 639.

compressibility $\phi(K_2)$ becomes greater the smaller the concentration, and it is necessary therefore to have very accurate data for the compressibility coefficients of dilute solutions in order to be able to calculate $\phi(K_2)$ with accuracy.

The best measurements¹ have been made using a principle first introduced by Debye and Sears.² They showed that light transmitted at right angles to a supersonic vibration, excited in the liquid by means of a high-frequency quartz plate oscillator, is resolved into spectra of different orders as if the liquid were behaving as a grating. For monochromatic light, the fringes are equidistant, and from the separation of these the ratio of the wave-length of light in air to the wave-length of the supersonic vibrations can be determined. The frequencies of the supersonic vibrations depend on the compressibility coefficients of the liquids and the values of these may therefore be obtained. The results show that the apparent molar compressibility is proportional to the square root of the concentration only for dilute solutions of strong electrolytes of the uni-univalent and uni-divalent types, while for electrolytes of higher valency types the observed slopes are less than those predicted from the interionic attraction theory. Gucker's hypothesis that non-electrolytes should also show a linear relation between the apparent molar compressibility and the square root of the concentration has, however, not been confirmed by measurements on cane-sugar solutions using the supersonic method.

The square-root relation which is also observed in the other apparent molar properties of strong electrolytes, such as heats of dilution and the partial molar volumes,³ follows readily from the Debye-Hückel analysis for reversible processes in electrolytes. The partial molar free energy is from equation (297),

$$\bar{F}_2 - \bar{F}_2^0 = (\sum_i n_i)RT \ln c - 2RT \frac{e^3 \mu^3}{(DkT)^{3/2}} \sqrt{\frac{\pi N}{1000}} \cdot \sqrt{c} \quad (126)$$

¹ Falkenhagen and Bachem, *Z. Electrochem.*, **41** (1935), 570; *Nature*, **135** (1935), 830.

² Debye and Sears, *Proc. Nat. Acad. Wash.*, **18** (1932), 402.

³ Gucker, *Chem. Rev.*, **13** (1933), 111.

Here, n_i is the number of ions of charge z_i and μ is the valency factor $\frac{1}{2}\sum_i n_i z_i^2$. If the partial molar free energy in (126) be differentiated with respect to pressure, it gives :

$$\frac{\partial^2}{\partial P^2}(\bar{F}_2 - \bar{F}_2^0) = \frac{\partial}{\partial P}(\bar{V}_2 - \bar{V}_2^0) = -(\bar{K}_2 - \bar{K}_2^0) \quad (127)$$

where $\bar{K}_2$ denotes the partial molar compressibility. The theoretical expression for the compressibility obtained in this way from equation (126) is

$$\bar{K}_2 - \bar{K}_2^0 = \frac{A}{\sqrt{2}} \mu^{\frac{1}{2}} f(V, D, P) c^{\frac{1}{2}} \quad . \quad . \quad (128)$$

where $f(V, D, P)$ is a complicated expression which may be written in terms of the dielectric constant, the pressure, and the compressibility coefficient. The variation of the dielectric constant with pressure has been determined experimentally,¹ and by substituting the values for the appropriate constants, equation (128) becomes, for aqueous solutions

$$\bar{K}_2 - \bar{K}_2^0 = 3.23 \times 10^{-4} \mu^{\frac{1}{2}} \sqrt{c} \text{ c.c. per bar} \quad . \quad (129)$$

The Debye-Hückel theory therefore predicts a square-root relation between the concentration and the partial molar compressibility in agreement with the experimental data which have been accumulated. It is, however, rather remarkable that the relation holds up to relatively high concentrations, over a range where the expressions for the other thermodynamic properties and for the conductivity break down completely. Although the observed slopes of the lines are in many cases not in good agreement with the calculated values, this may be due to the high degree of uncertainty in the values of the terms in $f(V, D, P)$.

Viscosities and Compressibilities in Non-electrolytes.

The square root of the concentration relation which has been observed in dilute solutions for so many properties of strong electrolytes is associated with the existence of the ion atmosphere, and in solutions of non-electrolytes the square-root relation would be expected to disappear. Relatively

¹ Falkenberg, *Ann. Physik*, 61 (iv) (1920), 145.

few measurements of the above properties for non-electrolytes are available, but for urea and sucrose the viscosities have been shown to be accurately linear with concentration,¹ while the apparent molar compressibilities of these substances do vary with the square root of the concentration in exactly the same way as for electrolytes.² A possible explanation of this anomaly is that ion-solvent and solvent-solute forces play a predominating part in the compressibility of solutions. This may result in a variation of the compressibility with concentration which, accidentally, coincides with that predicted from interionic forces alone. If this were the case, the difference between electrolytes and non-electrolytes would disappear, since the presence of the ion atmosphere would have practically no effect on the compressibility. The wide range over which the square-root law predicts the compressibilities of strong electrolytes satisfactorily would therefore be explained.

The Molar Volumes of Electrolytes.

It is at once apparent from equations (126) and (151)—viz.,

$$\frac{\partial}{\partial P}(\bar{V}_2 - \bar{V}_2^0) = \bar{V}_2 - \bar{V}_2^0$$

that the partial molar volumes of electrolytes should, according to the Debye-Hückel theory, vary linearly with the square root of the concentration. Thus we have :

$$\bar{V}_2 = \bar{V}_2^0 + a\mu^{\frac{1}{2}}\sqrt{c} \quad . \quad . \quad . \quad (130)$$

where $\bar{V}_2^0$ is the partial molar volume at infinite dilution. Observations of the apparent molar volumes of salts in aqueous solutions, which do not differ greatly from the partial molar volumes except in very strong solutions, show that the square-root law is obeyed very well,³ and like the partial molar compressibilities, may be applied at concentrations far higher than those at which the interionic theory can at present be applied. From a knowledge of the

¹ Jones and Talley, *J. Amer. Chem. Soc.*, **55** (1933), 624.

² Perman and Urry, *Proc. Roy. Soc., A*, **126** (1929), 44.

³ Masson, *Phil. Mag.*, **8** (vii) (1929), 218.

Geffcken, *Z. Physikal. Chem. (A)*, **155** (1931), 1.

constants in (126) and the variations of D with P , it is possible to calculate the values of " a " in equation (130), although the limiting slopes cannot be estimated from the experimental results.¹ The agreement between the calculated values and those obtained from the experimental data at moderate concentrations, is surprisingly good in view of the uncertainties in the variations of the dielectric constant with pressure and temperature.

Surface Tensions of Electrolytes.

The surface tension property of solutions of electrolytes has also recently been interpreted theoretically by means of the interionic attraction theory.² If it is assumed that the surface tension of a solution differs from that of a pure solvent only as a result of ion-ion forces, then the interionic attractions would result in a deficiency of ions in the surface layers, and consequently in an increase in the surface tension. As would be expected, the theory predicts that all electrolyte solutions of the same valency type should give identical surface tension-concentration curves. The form of the expression obtained for the variation of surface tension with concentration is complicated, but for aqueous solutions of uni-univalent electrolytes it may be written :

$$\frac{\sigma_c}{\sigma_o} = 1 + \frac{A}{D\sigma_o} c \log \frac{B(DT)^3}{c} \quad . \quad . \quad (131)$$

where σ_c is the surface tension of the solution at a concentration c , σ_o is the surface tension of the pure solvent, and A and B are constants. It follows from equation (131) that, at zero concentration, the relative surface tension curve should have a slope of infinity (positive), followed by a sharp negative curvature as the concentration rises. At a low concentration the curve turns to a gentle positive gradient which decreases until, at $c = 0.54$ for aqueous solutions, the relative surface tension has reached a maximum. The theory, however, cannot be expected to hold at such high concentrations, and a verification of the

¹ Redlich and Rosenfeld, *Z. Physikal. Chem. (A)*, **155** (1931), 65.

² Wagner, *Physikal. Z.*, **25** (1924), 474.

Onsager and Samares, *J. Chem. Phys.*, **2** (1934), 548.

equation can therefore only be made for the lower concentrations.

There are unfortunately great difficulties in measuring the static surface tension of solutions with a high degree of accuracy, and any method which is to be used for verifying the above equation must be a differential one. Heydweiller¹ first measured the surface tension sufficiently accurately to enable him to reach definite conclusions about the change of surface tension with concentration. Grinnell Jones and Ray² have obtained the best results using a capillary-rise method. In their arrangement the meniscus

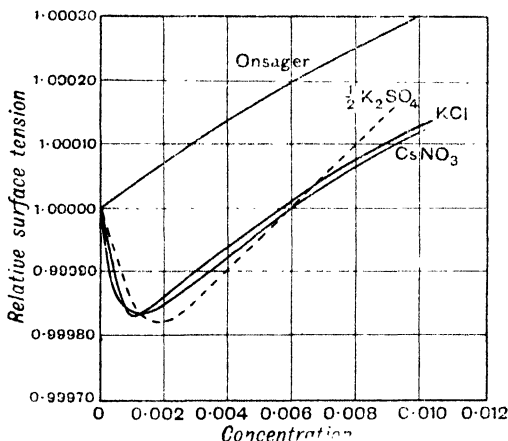


FIG. 49.—SURFACE TENSION VARIATIONS FOR SOME ELECTROLYTES.

of the liquid is always brought to the same level, thus avoiding the errors which might arise from a cathetometric measurement of a rise in level in a narrow tube and, at the same time, eliminating the influence of irregularities in the capillary bore. With this method Jones and Ray claim that they reduce experimental error to only 0.002% average deviation. Their results, however, show that the limiting slopes, instead of being positively infinite, are very large in the negative sense—i.e., that there is an initial decrease in relative surface tension. This is followed by the steady positive slope predicted by Onsager, but there is no corre-

¹ Heydweiller, *Ann. Physik*, **33** (iv) (1910), 145.

² Grinnell Jones and Ray, *J. Amer. Chem. Soc.*, **59** (1937), 187.

sponding maximum which the interionic theory predicts at a concentration of about $N/2$ for uni-univalent salts (see Fig. 49). It was first suggested that the lowering of the surface tensions observed in very dilute solutions could be explained by the effect which dissolved ions have on the water dipoles in breaking up the arrangement of the latter near the surface when there is positive adsorption of the substance. This explanation of the observed facts overlooks, however, the interaction between ions and water dipoles which produces a repulsion of ions, and hence a negative adsorption, at the surface.

In order to account for the initial positive adsorption, Dole¹ assumes that at certain parts of the water surface, configurations occur in which all the proton ends of adjacent water molecules are pointing inwards, where negative ions can be adsorbed. When all these adsorbing points are occupied, the minimum of the surface tension will be reached, and at higher concentrations the interionic forces become sufficiently great to account for the positive slope of the surface tension curve as in Onsager's theory. Following the procedure used by Langmuir for the adsorption of gases, an equation is first derived for θ , the fraction of adsorbing points in the water surface, actually covered. For negative ions, of which a number n_- are formed from the dissociation of 1 molecule of salt, the excess number of gram-molecules of negative ions adsorbed per sq. cm. is :

$$\Gamma_- = a\theta - cn_-k \quad . \quad . \quad . \quad (132)$$

where k is proportional to the thickness of the surface adsorption layer, c is the concentration in gram-moles per litre, and a is the number of active adsorbing spots per sq. cm. (expressed in gram-moles). A similar equation is obtained for adsorption of positive ions after allowing for the fact that θ is determined only by the concentration of negative ions. Now, from the Gibbs adsorption isotherm :

$$d\sigma = \sum_i \Gamma_i RT d \ln c_i f_i \quad . \quad . \quad . \quad (133)$$

where f_i is the activity coefficient, substitution may be made

¹ M. Dole, *J. Amer. Chem. Soc.*, **60** (1938), 904.

for the values of Γ_i and the equation for $d\sigma$ integrated from $c = 0$ to $c = c$, giving for low concentrations ($f_i \approx 1$):

$$\frac{\sigma}{\sigma_0} = 1 + \frac{RTk(n_- + n_+)c}{\sigma_0} + \frac{aRT(n_- + n_+)}{\sigma_0 n} \ln \left[1 + \frac{cn_- k}{ae^{W_-/RT}} \right] \quad (134)$$

W_- is the adsorption potential of negative ions per mole and it occurs in the equation for θ . Since the activity coefficient occurs in the Gibbs isotherm, the equation for the relative surface tension should be corrected for f_i before integrating, but the effect is only important at concentrations greater than that at which the minimum surface tension occurs. The equation predicts that the minimum should occur at the same concentration for salts of the same valency type, and it agrees well with the experimental results which have been obtained at low concentrations, not exceeding 0.02N.

CHAPTER VI

THE PRINCIPLES OF CHEMICAL THERMODYNAMICS

HITHERTO we have considered only non-stationary processes in electrolytes, and it has been seen that a satisfactory explanation of the behaviour of very dilute solutions can be given by applying the ordinary laws of hydrodynamics, after allowing for the effects of the ion atmospheres which move with the ion through the solution. We must now discuss the question of how the ion-atmosphere theory will account for the thermodynamic properties of solutions of strong electrolytes, and for the differences in behaviour which these show when they are compared with solutions of non-electrolytes of the same concentration. But first it will be necessary to give an outline of the principles of chemical thermodynamics and their applications to solutions.

The First Law of Thermodynamics.

Classical thermodynamics is based upon two laws. The first is a generalised form of the law of conservation of energy, and it states that

“the total energy of a system, distributed among all its conceivable functions such as heat, mechanical energy of motion, or radiation, is conserved during any changes within that system.”

The law has been verified experimentally with a high degree of precision in the measurements of Joule, Callendar and Barnes, etc. For any infinitesimal change it may be stated algebraically as follows :

$$dQ = dU + dW \quad . \quad . \quad . \quad (135)$$

Here Q is the total energy of the system (molecular heat content of Lewis), U is the internal energy (Lewis's E),

and W is the external work done *on* the system. In a system at constant pressure, for which an increase in total energy dQ is accompanied by an increase in volume dV , the external work done

$$dW = PdV \quad . \quad . \quad . \quad (136)$$

is
$$(dQ)_p = dU + PdV \quad . \quad . \quad . \quad (137)$$

If the system is maintained under conditions of constant volume, however, there is no external work of expansion during the energy changes and

$$(dQ)_v = dU \quad . \quad . \quad . \quad (138)$$

An example of the difference in magnitude which should be observed when a change takes place under different imposed conditions is provided by the thermochemical data for chemical reactions. These differ according as the reactions are carried out at constant pressure or at constant volume. As chemical reactions normally take place at constant pressure, the data are always tabulated as total heat contents (total energy changes) and are given by the equation

$$\int dH = \int dU + P \int dV$$

The Second Law of Thermodynamics.

“Every system which is left to itself will, on the average, change towards a state of maximum probability.”¹ (*i.e.*, towards a state of complete disorganisation).

The second law, unlike the first, is not capable of direct experimental confirmation. It is merely a statement of experience, and there are many other ways in which it may be expressed than that given above. The state of maximum probability referred to in Lewis's statement of the law defines the “equilibrium” of the system. At equilibrium a system will not move away from this state except under the influence of external agencies, and the path which the system has traversed in reaching the equilibrium point is

¹ G. N. Lewis and M. Randall, “Thermodynamics,” New York, 1923, p. 127.

therefore irreversible. This irreversibility in a spontaneous change implies a dissipation or degradation of energy, so that the maximum available energy is never obtained as work. But, although every actual system encountered in experience is irreversible, it is quite possible to conceive of a system in which all sources of the dissipation of energy are eliminated. Processes operated upon such a system are said to be completely reversible, and they must be imagined so to be carried out that, proceeding by infinitesimal steps, the system is restored to equilibrium after each step before proceeding to the next. There is therefore equilibrium at every stage of a reversible process. Now, this principle of reversibility, which has to be used in making all our thermodynamic derivations, is never quite realised in practice, but it is possible, especially in electrolytic systems, to approach it very closely. If, for example, an E.M.F. is applied between the two electrodes of a silver concentration cell,¹ the applied potential difference, which represents the imposed external effects, may then be so adjusted that, while opposite in direction to that of the cell, it differs in magnitude from it by as little as 0.000001 volt. A detectable current now flows through the cell in one direction, but a change in the applied E.M.F. of the order of 10^{-6} volt will alter the direction in which the current flows. Such a system, therefore, almost conforms to the principle of reversibility.

Entropy and Irreversibility.

The quantitative measure of the extent to which a system is irreversible is defined as the entropy of the system. For a reversible process the total entropy change must therefore be zero.

Like the energy, pressure, or volume changes, entropy change is determined only by the initial and final states of the system, and is independent of the particular path by which the final state is reached. Since the dissipation of energy also depends on the irreversibility of a system, the

¹ A silver concentration cell consists of two silver electrodes dipping into two solutions of, say, silver nitrate of different concentrations, the two solutions being brought into direct electrical contact in such a way that diffusion is reduced to a minimum.

entropy S may be represented as the rate at which energy is lost from the system per degree change in temperature :

$$dS = \frac{dQ}{T} \quad . \quad . \quad . \quad . \quad . \quad (139)$$

It must be noted here that we are concerned only with the infinitesimal entropy change in the system, which is the same whether the change is conducted reversibly or irreversibly. In the evaluation of

$$\Delta S = \int \frac{dQ}{T} \quad . \quad . \quad . \quad . \quad . \quad (140)$$

the right-hand side must, however, be calculated for a reversible change. For an irreversible change in one part of a system, less than the maximum work is obtained, and hence

$$\int dQ = \int dU + \int dW \quad . \quad . \quad . \quad (141)$$

is smaller—i.e., $\int \frac{dQ}{T}$ is less than for a reversible process.

Provided the heat absorbed by this part of the system comes from the remainder of the system at the same temperature and is transferred reversibly, the entropy loss of the remaining part of the system is equal to $\int \frac{dQ}{T}$. Thus the total entropy change of the system consequent upon the irreversible process which has occurred in one part of the system, is positive. We may therefore say that in any system in which an irreversible change takes place, the entropy increases. For a system not in equilibrium we have seen that the probability tends to proceed to a maximum, and hence entropy and probability should be related. Boltzmann has in fact shown ¹ that

$$S = -K \log P \quad . \quad . \quad . \quad . \quad (142)$$

The Thermodynamic Functions A and F.

From equations (135) and (139) we see that

$$dQ = dU + dW = TdS \quad . \quad . \quad (143)$$

¹ Born, "Atomic Physics," London, 1935, pp. 332-334.

Now, for the solution of these equations a third equation is required, since there are three independent variables Q , U , and S . This is supplied by one of the equations of Massieu which define the characteristic quantities A and F . These may be used in place of the entropy to denote the tendency of a system to undergo spontaneous change and, in terms of the variables already employed, they are defined ¹ by

$$A = U - TS \quad . \quad . \quad . \quad . \quad . \quad (144)$$

$$F = U - TS + PV = H_p - TS \quad . \quad (145)$$

where H_p is the heat content of the system under conditions of constant pressure. In equations (144) and (145), A is defined under constant temperature conditions, F with pressure and temperature as constants and volume as the independent variable. Since most chemical changes take place under conditions of constant temperature and pressure, it is more usual to employ F for describing the thermodynamics of the reactions. A and F are both expressed explicitly in terms of factors which are themselves properties of the system. In this sense A and F may be called thermodynamic functions of the state of the system.

For any reversible change the magnitude of which is of the first order of small quantities, we have ² at constant pressure :

$$dH_p = TdS \quad . \quad . \quad . \quad . \quad (146)$$

Also from (145), by differentiation without regard to the conditions :

$$dF = dU + PdV + VdP - TdS - SdT \quad . \quad (147)$$

The two laws of thermodynamics (equation 143) give :

$$dU - TdS + PdV = 0 \quad . \quad . \quad (148)$$

and hence
$$dF = VdP - SdT \quad . \quad . \quad . \quad (149)$$

At constant pressure, therefore,

$$\left(\frac{\partial F}{\partial T}\right)_p = -S \quad . \quad . \quad . \quad . \quad (150)$$

¹ Massieu, *Compt. Rend.*, **59** (1869), 858, 1057.

² It will be realised that, for chemical reactions where Q becomes equal to the heat content, we write H for Q .

while at constant temperature

$$\left(\frac{\partial F}{\partial P}\right)_T = V \quad . \quad . \quad . \quad . \quad (151)$$

From equation (151) we can obtain further information about the nature of the function F . For, if a system undergoes a finite reversible change from a state A to a state B , then, denoting the difference in F for the two states by ΔF , we have

$$\Delta F = F_{II} - F_I = \int_I^{II} V dP \quad . \quad . \quad . \quad (152)$$

The function F , therefore, has the dimensions of work, since it is a measure of the maximum work obtainable from a system under the appropriate conditions. It is called the free energy of the system in the given state. Its absolute value in any state has not been defined, and its value for a particular state must therefore be expressed as the difference between its values for that state and for some standard state. The function A (*arbeit*) also has the dimensions of work, and it is named after its originator the "Helmholtz free energy." Since from (144) and (145)

$$F = A + PV,$$

any expression derived from the one function may immediately be transformed into an expression involving the other.

The Gibbs-Helmholtz Equation.

For a change in a system from state I to II, where the free energy change is

$$\Delta F = F_2 - F_1$$

equation (150) gives us :

$$\left(\frac{\partial \Delta F}{\partial T}\right)_p = \Delta S \quad . \quad . \quad . \quad . \quad (153)$$

Also from equation (145)

$$\Delta F = \Delta H_p - T\Delta S \quad . \quad . \quad . \quad (154)$$

i.e.,

$$\Delta S = \frac{\Delta F - \Delta H_p}{T} \quad . \quad . \quad . \quad (155)$$

and substituting for ΔS in (153), we have the well-known Gibbs-Helmholtz equation :

$$\Delta F - \Delta H_p = T \left(\frac{\partial \Delta F}{\partial T} \right)_p \quad . \quad . \quad (156)$$

It is usual to write the equation as

$$F - H = T \left(\frac{\partial F}{\partial T} \right)_p \quad . \quad . \quad . \quad (157)$$

and to remember that the functions F and H refer here to the difference in free energy and heat content of the system at constant pressure over the range considered. By differentiating $\left(\frac{F}{T} \right)$ with respect to T , we have :

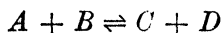
$$T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right)_p = - \left[F - T \left(\frac{\partial F}{\partial T} \right)_p \right] \quad . \quad . \quad (158)$$

or, comparing this with (157) :

$$\frac{\partial}{\partial T} \left(\frac{F}{T} \right)_p = - \frac{H_p}{T^2} \quad . \quad . \quad . \quad (159)$$

The Free Energy of Chemical Reaction.

The value of the free energy change in a chemical reaction which is proceeding from some initial state to equilibrium may be calculated by van 't Hoff's equilibrium box method. We will consider a simple reversible reaction :



supposed to be carried out in the gaseous phase throughout, and we will denote the initial and final concentrations of A and B by $[A]_i$, $[B]_i$; the final concentrations of the products by $[C]_f$ and $[D]_f$; and the equilibrium concentrations of all the species of $[A]_e$, $[B]_e$, $[C]_e$, $[D]_e$. When concentrations are replaced by their corresponding activities,¹ square brackets will be replaced by ordinary parantheses, thus $(A)_e$. The equilibrium box (Fig. 50) is an arrangement whereby the reactants and products may be added to or removed from

¹ It is supposed that the reader has some knowledge of the meaning of activity. A fuller account of this is given in the subsequent sections in this chapter.

the sphere of reaction, iso-thermally and reversibly, each through one of the perfectly semi-permeable, frictionless pistons, which give access to the reaction chamber. We will suppose for a first consideration that all the concentrations are sufficiently low for the components to obey the perfect gas law throughout. In conducting the reaction, A and B are first expanded iso-thermally and reversibly from their

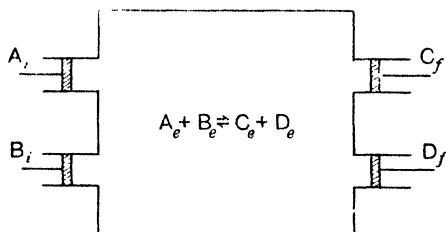


FIG. 50.—VAN 'T HOFF'S EQUILIBRIUM BOX.

initial to their equilibrium concentrations. For each component the maximum work is obtained in this way, since the changes are reversible and the total work *done* is therefore

$$F_A + F_B = \int_i^e (PdV)_A + \int_i^e (PdV)_B \quad . \quad (160)$$

Remembering that for a perfect gas

$$\begin{aligned} PV &= RT \\ P &= CRT \end{aligned}$$

we have :

$$\int_i^e (PdV)_A = RT \int_i^e \left(\frac{dV}{V} \right)_A = RT \ln \frac{[A]_e}{[A]_i} \quad (161)$$

$$\text{i.e.,} \quad F_A + F_B = RT \ln \frac{[A]_e}{[A]_i} + RT \ln \frac{[B]_e}{[B]_i} \quad . \quad (162)$$

Now that the reacting gases are at their equilibrium concentrations, the reaction is able to proceed without any work being done on or by the system. The products must be brought to their final concentrations through their permeable pistons in order to complete the process. During these stages an amount of work

$$F_C + F_D = RT \ln \frac{[C]_f}{[C]_e} + RT \ln \frac{[D]_f}{[D]_e} \quad . \quad (163)$$

is obtained from the system. Thus the maximum work *obtained* from the reaction, which is equal to the free energy of the chemical reaction, is :

$$F = -F_A - F_B + F_C + F_D \quad . \quad . \quad (164)$$

$$\text{or } F = -RT \ln \frac{[A]_e}{[A]_i} - RT \ln \frac{[B]_e}{[B]_i} + RT \ln \frac{[C]_f}{[C]_i} + RT \ln \frac{[D]_f}{[D]_e}$$

$$\text{i.e. } F = RT \ln \frac{[C]_f[D]_f}{[A]_e[B]_e} + RT \ln \frac{[C]_i[D]_i}{[A]_i[B]_i} \quad . \quad . \quad . \quad (165)$$

Also the equilibrium constant K_e expressed on the concentration scale is :

$$K_e = B \frac{[C]_e[D]_e}{[A]_e[B]_e} \quad . \quad . \quad . \quad (166)$$

and writing :

$$RT \ln \frac{[C]_f[D]_f}{[A]_e[B]_e} = \Sigma RT \ln c \quad . \quad . \quad (167)$$

substitution of (166) and (167) in (165) gives us the expression for the free energy :

$$F = -RT \ln K_e + \Sigma RT \ln c \quad . \quad . \quad (168)$$

If concentrations are replaced throughout by the corresponding activities, the equation will read :

$$F = -RT \ln K_a - \Sigma RT \ln a \quad . \quad . \quad (169)$$

where

$$K_a = \frac{(C)_e(D)_e}{(A)_e(B)_e} \quad . \quad . \quad . \quad (170)$$

If the initial and final concentrations (or activities) are arranged to be unity, the term $\Sigma RT \ln c$ becomes zero and

$$F = -RT \ln K_e \quad . \quad . \quad . \quad (171)$$

Substituting for F in (159), we have the van 't Hoff equation :

$$\frac{\partial \ln K_e}{\partial T} = \frac{H_p}{RT^2} \quad . \quad . \quad . \quad (172)$$

If the variation of the heat of reaction H_p with the temperature is known, the equilibrium constant may therefore be calculated at any temperature, provided it is possible to evaluate the integration constant. The change of the

heat of reaction of gaseous reactions with temperature may be expressed arbitrarily as a series in temperature

$$H_p = H_0 + \alpha T + \beta T^2 + \gamma T^3 + \dots \quad (173)$$

by a suitable choice of the constants α , β , γ , ... Thus substituting into (172) we have :

$$\frac{\partial \log K_c}{\partial T} = \frac{H_0}{RT^2} + \frac{\alpha}{RT} + \frac{\beta}{R} + \frac{\gamma T}{R} + \dots \quad (174)$$

which by integration gives :

$$\ln K_c = -\frac{H_0}{RT} + \frac{\alpha}{R} \ln T + \frac{\beta T}{R} + \frac{\gamma T^2}{2R} + \dots + J \quad (175)$$

where J is the integration constant. Since also from (171)

$$F = -RT \ln K_c$$

we have :

$$F = H_0 - \alpha T \ln T - \beta T^2 - \frac{\gamma T^3}{2} \dots - IT \quad (176)$$

where the new integration constant $I = JR$. Equation (176) gives the variation of the free energy of a reaction with temperature, provided the value of I can be obtained.

The Choice of a Standard State and the Activity.

Since free energy can only be measured by difference, it is desirable to define a common standard state for all free energy values. In order to accomplish this, Lewis¹ expressed the difference ($F_{II} - F^0$) between the free energy of the system in a given state, and that in the standard state, as a function of an arbitrary variable of the system which he called the activity. If this has a value a in the measured state, then by definition, a is given by

$$F_{II} - F^0 = RT \ln a_{II} \quad (177)$$

The choice of the standard state will therefore depend on the properties of the function a , and the nature of this must first be investigated. From the definition of free energy it was found (equation 152) that, for a reversible change in a system, from states I to II,

$$\Delta F = \int_I^{II} V dP \quad (178)$$

¹ Lewis, *Proc. Amer. Acad.*, **43** (1907), 259.

For a perfect gas, or for an ideal solution, the pressure and volume of the one, or the osmotic pressure and the concentration of the other, are connected by the respective equations:

$$\left. \begin{aligned} PV &= RT \\ P &= CRT \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (179)$$

where C is the concentration on some arbitrary scale, and therefore

$$\Delta F = \int_I^{II} \frac{RT}{P} dP = RT \ln \frac{P_{II}}{P_I} = RT \ln \frac{C_{II}}{C_I} \quad (180)$$

at constant temperatures. If state I be the standard state for which the free energy is F^0 , we have from (180):

$$F_{II} - F^0 = RT \ln \frac{P_{II}}{P_I} = RT \ln \frac{P_{II}}{C_I} \quad . \quad (181)$$

Comparing this with (177) we have an expression for the activity of the system in state II , viz.:

$$a_{II} = \frac{P_{II}}{P_I} = \frac{C_{II}}{C_I} \quad . \quad . \quad . \quad . \quad (182)$$

This equation, however, is valid only if the substance in the gaseous state or in solution, be sufficiently attenuated to allow the limiting equation

$$PV = RT$$

to be applied, and it will cease to be valid, therefore, at all but the lowest concentrations. At high concentrations intermolecular forces become appreciable, and if the gas equation is still to be applied, they must be accounted for by an additional term. In the simplest case it may be supposed that the repulsive force between two molecules separated by a distance r is a function $\phi(r)$ of the distance only. It is then easy to calculate the contribution of intermolecular forces to the virial of the substance, which is found to be $\frac{1}{2} \sum v \phi(r)$.¹ The summation in this additional

¹ For Debye-Hückel electrolytes, the virial for a mixture of ions may be calculated by neglecting ion solvent forces and assuming a Coulomb law to give the attractions and repulsions between the ions (S. R. Milner, *Phil. Mag.*, **23** (vi) (1912), 551; *ibid.*, **25** (vi) (1913), 742).

term must be taken over all possible pairs of molecules. At finite pressures, therefore, equation (179) becomes : ¹

$$PV = \frac{1}{3}\Sigma m\bar{c}^2 + \frac{1}{2}\Sigma v\phi(r) \quad . \quad . \quad (183)$$

where $\bar{c}$ is the root mean square velocity of the molecule. A solution of equation (183), and hence of the expression (182), for the activity, is only possible, therefore, when the exact nature of the function $\phi(r)$ is known at all densities.

Activity Coefficients.

Equation (182) may, however, be modified in another way so that it applies at all concentrations by writing :

$$a_{II} = \frac{f_{II} c_{II}}{f_I c_I}$$

where f_{II} and f_I are *adjustable* constants chosen to fit the equality at any concentration. The f 's, which are called activity coefficients, are, of course, themselves functions of the concentration.² Now, since concentrations are defined by different conventions—e.g., molar fractions, gram-moles per litre of solution or gram-moles per 1000 gms. of solvent—the activity coefficient f will also have different values for the same numerical concentration according to the convention employed in measuring the concentrations. Molar fractions η_i are most commonly employed as a concentration scale in thermodynamics and the activity coefficients f_{η_i} referred to this system are called “rational activity coefficients.” When the concentrations are measured in gram-moles per litre of solution (γ_i) or per 1000 gms. of solvent (m_i) the corresponding activity coefficients f_{γ_i} and f_{m_i} are called “practical activity coefficients.” f_{m_i} and f_{γ_i} will differ from f_{η_i} by factors depending on the relation between m_i , γ_i and η_i .³ These relations may easily be obtained from the definitions of the concentration scales. For, if there are present $N_1 \dots N_i \dots N_s$ molecules respectively of the species 1 . . .

¹ J. H. Jeans, “Dynamical Theory of Gases” (Cambridge 1925), 130.

² Lewis and Randall, *J. Amer. Chem. Soc.*, **43** (1921), 1112.

³ E. Hückel, *Physikal. Z.*, **26** (1925), 93.

A. MacFarlane and O. Gatty, *Phil. Mag.*, **13** (vii) (1932), 283, 291.

E. A. Guggenheim, *ibid.*, **19** (vii) (1935), 588.

$i \dots s$, and if N be Avogadro's number, the numbers of moles of each species present are :

$$\frac{N_1}{N} \dots \frac{N_i}{N} \dots \frac{N_s}{N}$$

Putting N_0 for the number of molecules of solvent present, the molar fractions are therefore given by expressions of the type :

$$\eta_i = \frac{N_i}{N_0 + \sum_s N_i} = \frac{\frac{N_i}{N}}{\frac{N_0}{N} + \sum_s \frac{N_i}{N}} \quad \dots \quad (185)$$

In the concentrations in gram-moles per litre of solution we have expressions :

$$\gamma_i = \frac{N_i}{NV} \cdot 1000 \quad \dots \quad (186)$$

where V is total volume of the solution in c.c., and, finally, the concentrations of the solutions expressed as gram-moles per 1000 gms. of solvent are given by :

$$m_i = \frac{\frac{N_i}{N}}{\frac{N_0 M_0}{N}} \cdot 1000 \quad \dots \quad (187)$$

where M_0 is the molecular weight of the solvent. The density of the solution D which is its mass per unit volume will be

$$D = \frac{\frac{N_0 M_0}{N} + \sum_s \frac{N_i M_i}{N}}{V} \quad \dots \quad (188)$$

From these four equations we may obtain the following relations between the different concentration conventions :

$$\left. \begin{aligned} \gamma_i &= \frac{m_i D}{1 + \sum_s \frac{N_i m_i}{1000}} \\ m_i &= \frac{\gamma_i}{D - \sum_s \frac{M_i \gamma_i}{1000}} \\ \eta_i &= \frac{M_0 \gamma_i}{1000} \cdot \frac{1}{D - \sum_s \frac{(M_i - M_0) \gamma_i}{1000}} = \frac{N_0 m_i}{1000} \cdot \frac{1}{1 + M_0 \sum_s \frac{m_i}{1000}} \end{aligned} \right\} \quad (189)$$

In general, therefore, the concentration scales are not strictly proportional to one another at different concentrations.

Since the activity is itself independent of any concentration scale we have :

$$a = \eta_i f_{\eta_i} = \gamma_i f_{\gamma_i} = m_i f_{m_i} \quad . \quad . \quad . \quad (190)$$

which with equations (189) gives the required relations between the activity coefficients, viz. :

$$\left. \begin{aligned} f_{\gamma_i} &= f_{\eta_i} \cdot \frac{M_0}{1000} \cdot \frac{1}{D - \sum_s \frac{(M_s - M_0)\gamma_s}{1000}} \\ f_{m_i} &= f_{\eta_i} \cdot \frac{M_0}{1000} \cdot \frac{1}{1 + M_0 \sum_s \frac{m_s}{1000}} \end{aligned} \right\} \quad . \quad (191)$$

It would be a matter of convenience if f_{m_i} and f_{γ_i} , the practical activity coefficients, could at low concentrations be made to approach the value which the rational activity coefficient then has. But from equations (189) the concentrations expressed by the three conventions become proportional to one another at low concentrations. In accordance with the equations

$$\eta_i = \frac{\gamma_i M_0}{1000 D_0} = \frac{m_i M_0}{1000} \quad . \quad . \quad . \quad (192)$$

where D_0 is the density of the solvent. Hence if at low concentrations we are to have :

$$f_{\eta_i} = f_{m_i} = f_{\gamma_i} \quad . \quad . \quad . \quad (193)$$

the following relations must hold :

$$f_{\eta_i} \frac{\eta_i M_0}{1000 D_0} = f_{\gamma_i} \gamma_i = f_{m_i} m_i \quad . \quad . \quad (194)$$

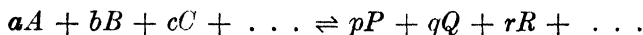
When, therefore, the activity coefficients are arranged to be equal at the limiting concentration, the practical coefficients must be obtained from the rational activity coefficients in dilute solutions, by multiplying by the factor $\frac{1000 D_0}{M_0}$.

The choice of the standard state for the measurement of activities and standard free energies is now possible, since

it will be that for which the activity coefficients are all unity. For solutions and gases it will be possible to apply the perfect gas law with complete accuracy to a system in the standard state—*i.e.*, the substance in these phases will be at infinite dilution. For a substance acting as a solvent, however, the standard state will be defined as that for which the concentration of the solute is infinitesimally small—*i.e.*, for which the molar fraction of the solvent is unity and of the solute is sensibly zero. For a binary solute the activity of the solute is therefore related to the concentration terms at all concentrations by the equation

$$a = \frac{fc}{c_0} \quad . \quad . \quad . \quad . \quad . \quad (195)$$

All the expressions which involve the concentration terms for the components of a system, and which only apply at limiting concentrations, may now be made valid at all concentrations by replacing the concentration terms by the activities. Thus the equilibrium constant for a general reaction



which, at limiting concentrations, may be expressed as

$$K_c = \frac{C_A^a C_B^b C_C^c}{C_P^p C_Q^q C_R^r}$$

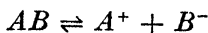
will, at finite concentrations, be given by

$$K_a = \frac{a_A^a a_B^b a_C^c}{a_P^p a_Q^q a_R^r} \quad . \quad . \quad . \quad . \quad . \quad (196)$$

which has exactly the same form as the original expression. K_a , however, is not the same as K_c .

The Activities and Activity Coefficients of Strong Electrolytes.

Since a strong electrolyte dissociates into ions, each of the species present may be supposed to have its own individual activity in the solution.¹ For a binary electrolyte for which the simple dissociation



¹ Lewis, *J. Amer. Chem. Soc.*, **34** (1912), 1631.

takes place, and for which the activities of the respective species are denoted by a_2 , a_+ and a_- , the mass law gives :

$$K_a = \frac{a_+ a_-}{a_2} \quad . \quad . \quad . \quad . \quad (197)$$

at a fixed temperature. For strong electrolytes, however, there is no exact knowledge of the value of the concentration of the undissociated part of the electrolyte, and the standard state is therefore so chosen that K_a in equation (197) is unity. Then

$$a_2 = a_+ a_- \quad . \quad . \quad . \quad . \quad (198)$$

Also, defining $a_{\pm}$ as the mean activity of the electrolyte, where

$$a_{\pm} = \sqrt{a_+ a_-} \quad . \quad . \quad . \quad . \quad (199)$$

it follows that :

$$a_{\pm} = \sqrt{a_2} \quad . \quad . \quad . \quad . \quad (200)$$

Since also for the electrolyte, the partial molar free energy $\bar{F}_2$ in solution is, from (177),

$$\bar{F}_2 = \bar{F}_2^0 + RT \ln a_2 \quad . \quad . \quad . \quad (201)$$

we have from (200) :

$$\bar{F}_2 = \bar{F}_2^0 + 2 RT \ln a_{\pm} \quad . \quad . \quad (202)$$

Similar relations to (199) may be obtained for the activity coefficients, for, assuming for the moment that the ions can have individual activity coefficients f_+ and f_- ,

$$\left. \begin{aligned} f_+ &= \frac{a_+}{c_+} \\ f_- &= \frac{a_-}{c_-} \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (203)$$

both of which approach unity as C_+ and C_- tend to their limiting values (zero). For the activity coefficient of the salt, an expression must be obtained which also approaches unity as the concentration decreases. Thus defining $f_{\pm}$, the mean activity coefficient of the electrolyte, as

$$f_{\pm} = \frac{a_{\pm}}{c_{\pm}} \quad . \quad . \quad . \quad . \quad (204)$$

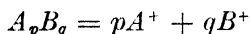
where

$$c_{\pm} = \sqrt{c_+ c_-}$$

we have from (203) and (204)

$$f_{\pm} = \sqrt{f_+ f_-} \quad . \quad . \quad . \quad (205)$$

This expression becomes equal to unity as this concentration tends to zero, since both f_+ and f_- separately are equal to unity then. For a more complex electrolyte which dissociates according to the scheme



it may easily be seen that the equations corresponding to (199) and (205) will be :

$$\left. \begin{aligned} a_{\pm} &= (a_+^p a_-^q) \frac{1}{p+q} \\ f_{\pm} &= (f_+^p f_-^q) \frac{1}{p+q} \end{aligned} \right\} \quad . \quad . \quad . \quad (206)$$

or, omitting the $\pm$ subscript for $a_{\pm}$ and $f_{\pm}$, and writing the equations more conveniently :

$$\left. \begin{aligned} (p+q) \log a &= p \log a_+ + q \log a_- \\ (p+q) \log f &= p \log f_+ + q \log f_- \end{aligned} \right\} \quad . \quad (207)$$

We have assumed throughout this discussion that the ions of an electrolyte in solution may be supposed to have individual ion activities and activity coefficients. These quantities, however, like the individual partial ionic free energies, have no thermodynamic significance,¹ and it is impossible to determine their absolute values. Any attempt to make an estimate of them would require the use of a liquid junction the value of which itself depended on the individual ion activities to be measured. Only the mean activity coefficients of electrolytes have any real thermodynamic significance and any convention may be adopted by the suitable choice of a value for one ionic species, for defining individual ion activity, provided it leads to the correct values for the mean activity coefficient of the electrolyte.²

¹ P. B. Taylor, *J. Physical Chem.*, **31** (1927), 1478.

E. A. Guggenheim, *ibid.*, **33** (1929), 842.

² Harned, "Electrochemistry of Solutions"; "Physical Chemistry," ed. Taylor, 1930, Vol. i, p. 820.

The Experimental Determination of the Activities and Activity Coefficients.

In the following section we shall consider a few of the more important methods which are available for the determination of the activity coefficients of substances, particularly of their electrolytes. No account is taken of the type of activity coefficient, rational or practical, which is involved, since this depends on the concentration scale which is chosen in making the measurements.

(a) Determinations of Activities from Vapour Pressures of the Substance.

The standard state in (182) has been defined so that, in that state, the substance is in infinite dilution. Thus, for very low concentrations we may write :

$$a = \frac{P_{\text{II}}}{P_0} \quad . \quad . \quad . \quad . \quad . \quad (208)$$

This equation suggests the possibility of determining the activity from the vapour pressure at different molar fractions. The method is limited to those substances which are sufficiently volatile for their vapour pressures to be measured easily. It has, however, been successfully applied to determine the activities of hydrogen halides in aqueous solutions at concentrations where the vapour pressure is measurable,¹ and of bromine in carbon tetrachloride solutions.² The procedure adopted for estimating the activities is as follows. At infinite dilution the vapour pressure P_0 of a pure solvent is constant at a given temperature and does not involve the molar fraction, which, for a pure solvent, is always unity. Equation (208) may therefore be written for the solute component II in the solution as

$$P_{\text{II}} = K a_{\text{II}} \quad . \quad . \quad . \quad . \quad (209)$$

where the constant K is determined by the fact that, when the solution is exceedingly dilute

$$P_{\text{II}} = K \eta_{\text{II}} \quad . \quad . \quad . \quad . \quad (210)$$

¹ D. J. Bates and Kirschman, *J. Amer. Chem. Soc.*, **41** (1919), 1991.

² Lewis and Storch, *ibid.*, **39** (1917), 2544.

η_{II} is here the molar fraction of the solute in the correct molecular state. The constant K may therefore be determined by constructing the tangent at the origin of curve (210). With this value of K the activity at any other partial vapour pressure P_{II} may be read off from the curve, using equation (209). The plot of equation (210) represents the extrapolation of Raoult's law from the region of very dilute solutions, and in Fig. 51 the way in which the curve for bromine in carbon tetrachloride falls below this line is very well illustrated. The extrapolation from the point B

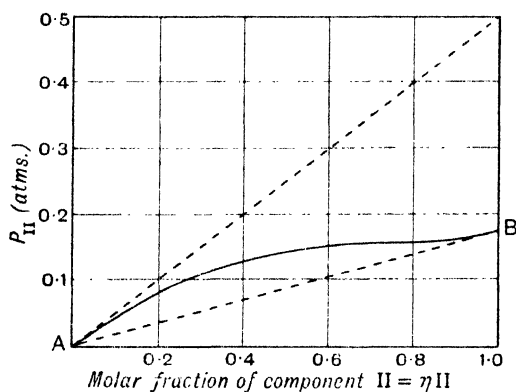


FIG. 51.—ACTIVITIES FROM VAPOUR-PRESSURE DATA.

on the right-hand side of the graph is that of the pressure molar fraction curve of the solvent, for when the molar fraction of bromine is η_{Br_2} , that of the solvent is $(1 - \eta_{Br_2})$.

(b) *Determination of Activities from Vapour Pressure of Solvent.*

When the system consists of a non-volatile solute dissolved in a volatile solvent, the method just described may be extended by determining the vapour pressure of the solvent and using the Gibbs-Duhem-Margules relation between the activities a_1 and a_2 of the solute and solvent components. This very valuable equation may be deduced as follows. If we suppose that there are n_1 moles of the first component for which the molar fraction is η_1 , and n_2

moles of the second for which the molar fraction is η_2 , then we have by definition

$$\eta_1 = \frac{n_1}{\sum n} \quad \eta_2 = \frac{n_2}{\sum n} \quad \dots \quad (211)$$

Also if F be the total free energy for the system¹ the partial molar free energies for the components are :

$$\left. \begin{aligned} \bar{F}_1 &= \left(\frac{\partial F}{\partial n_1} \right)_{T, P, n_2, n_3, \dots} \\ \bar{F}_2 &= \left(\frac{\partial F}{\partial n_2} \right)_{T, P, n_1, n_3, \dots} \\ &\vdots \\ \bar{F}_n &= \left(\frac{\partial F}{\partial n_n} \right)_{T, P, n_1, n_2, \dots} \end{aligned} \right\} \quad \dots \quad (212)$$

To simplify the analysis we shall consider now only a binary system. By the properties of partial differentials we have

$$\frac{\partial}{\partial n_2} \left(\frac{\partial F}{\partial n_1} \right)_{T, P, n_2} = \frac{\partial}{\partial n_1} \left(\frac{\partial F}{\partial n_2} \right)_{T, P, n_1} \quad \dots \quad (213)$$

or from (212)

$$\left(\frac{\partial \bar{F}_1}{\partial n_2} \right)_{T, P, n_1} = \left(\frac{\partial \bar{F}_2}{\partial n_1} \right)_{T, P, n_2} \quad \dots \quad (214)$$

Remembering that the partial molar free energies are always considered at constant temperature and pressure,

$$\left(\frac{\partial \bar{F}_1}{\partial \eta_2} \right) \left(\frac{\partial \eta_2}{\partial n_2} \right)_{n_1} = \left(\frac{\partial \bar{F}_2}{\partial \eta_1} \right) \left(\frac{\partial \eta_1}{\partial n_1} \right)_{n_2} \quad \dots \quad (215)$$

From (211) we have, for a binary system

$$\left. \begin{aligned} \left(\frac{\partial \eta_1}{\partial n_1} \right)_{n_2} &= \frac{n_2}{(n_1 + n_2)^2} = \frac{\eta_2}{n_1 + n_2} \\ \left(\frac{\partial \eta_2}{\partial n_2} \right)_{n_1} &= \frac{n_1}{(n_1 + n_2)^2} = \frac{\eta_1}{n_1 + n_2} \end{aligned} \right\} \quad \dots \quad (216)$$

Substituting for these differentials in (215)

$$\eta_2 \left(\frac{\partial \bar{F}_2}{\partial \eta_1} \right) = \eta_1 \left(\frac{\partial \bar{F}_1}{\partial \eta_2} \right) \quad \dots \quad (217)$$

¹ It should be noted that free energy is an extensive property—i.e., its value is dependent on the masses of the components present.

This equation is valid so long as the partial molar free energies are definite functions of the variables. From (177)

$$\bar{F}_2 = \bar{F}^0 + RT \ln a_2$$

and hence (217) becomes

$$\eta_1 \frac{\partial \ln a_1}{\partial \eta_2} = \eta_2 \frac{\partial \ln a_2}{\partial \eta_1} \quad . \quad . \quad . \quad (218)$$

This may be written more symmetrically by remembering that

$$\eta_1 = 1 - \eta_2$$

and that the operator $\frac{\partial}{\partial \eta_1}$ may therefore be replaced by $-\frac{\partial}{\partial \eta_2}$ in equation (218), giving

$$\eta_1 \frac{\partial \ln a_1}{\partial \eta_1} = \eta_2 \frac{\partial \ln a_2}{\partial \eta_2} \quad . \quad . \quad . \quad (219)$$

This equation, in which the activities of the two components appear, is valid whatever the molar fraction η_2 of the solute component. (219) may be written

$$\partial \ln a_1 = -\frac{\eta_1}{\eta_2} \partial \ln a_2 \quad . \quad . \quad . \quad (220)$$

After transforming to common logarithms and integrating between the two states, *A* and *B*, it becomes

$$(\log a_2)_A - (\log a_2)_B = \int_A^B \frac{\eta_1}{\eta_2} \partial \log a_1 \quad . \quad . \quad (221)$$

This equation is not convenient for extrapolating to infinite dilution, since the logarithmic terms on the left-hand side become large negative quantities. The equations may easily be transformed into the corresponding equation involving the activity coefficients by using the following relations

$$\left. \begin{aligned} \partial \ln \eta_2 &= \frac{\partial \eta_2}{\eta_2} = -\frac{\partial \eta_1}{\eta_1} \\ \partial \ln \eta_1 &= \frac{\partial \eta_1}{\eta_1} \end{aligned} \right\} \quad . \quad . \quad . \quad (222)$$

i.e.,

$$\partial \ln \eta_1 = -\frac{\eta_1}{\eta_2} \partial \ln \eta_2 \quad . \quad . \quad . \quad (223)$$

Subtracting (223) from (220) we have :

$$\partial \ln \frac{a_2}{\eta_2} = - \frac{\eta_1}{\eta_2} \partial \ln \frac{a_1}{\eta_1} \quad . \quad . \quad . \quad (224)$$

and, by converting to common logarithms and integrating between the two states *A* and *B*, (224) becomes

$$(\log f_2)_A - (\log f_2)_B = \int_A^B \frac{\eta_1}{\eta_2} \partial \log f_2 \quad . \quad . \quad (225)$$

With a knowledge of the molar fractions, integration is carried out graphically to give f_2 . The method has been applied to calculate the activity coefficient of potassium chloride in aqueous solutions,¹ and of sulphuric acid in mixtures of sulphuric acid and water.² Unfortunately the measurements are always least accurate at high dilutions where accurate values are necessary for comparing with the theory (see Chapter VII). For this reason the more accurate determinations from the E.M.F.'s of cells and the depressions of the freezing points have been more generally employed for estimating the activity coefficients.

(c) *Determinations of Activities from Electromotive Force Measurements.*

In a concentration cell consisting of two solutions of an electrolyte, for which the activities are a_1 and a_2 , each in contact with an electrode of the same metal as the cation present, the free energy change accompanying the transference of one gram ion of the metal of valency z from one solution to the other, is :

$$\bar{F}_1 - \bar{F}_2 = -\Delta\bar{F} = RT \ln \frac{a_1}{a_2} \quad . \quad . \quad (226)$$

By the first law of thermodynamics this must be equal and opposite to the electrical energy zEF supplied, *i.e.* :

$$\Delta\bar{F} = -RT \ln \frac{a_1}{a_2} = zEF \quad . \quad . \quad . \quad (227)$$

$$E = -\frac{RT}{zF} \ln \frac{a_1}{a_2} \quad . \quad . \quad . \quad . \quad (228)$$

¹ M. Randall and A. H. White, *J. Amer. Chem. Soc.*, **48** (1926), 2515.

² A. Grollmann and J. C. W. Fraser, *ibid.*, **47** (1925), 712.

Unfortunately it is rarely possible to obtain reproducible readings of the E.M.F. of a concentration cell in which the concentration of one of its solutions is so low that its activity may be put equal to its molar fraction. The procedure used is therefore as follows. The concentration of the solution expressed as a molar fraction is fixed at some value η_2' , let us say that for which the activity is equal to a_2' . This is so chosen that, within the range of concentrations of the solution, the E.M.F.'s will be of a magnitude convenient for experimental determination. From (228),

$$\ln a_1 = -\frac{zEF}{RT} + \ln a_2' . . . \quad (229)$$

Subtracting $\ln \eta_1$ from each side of (229), we have :

$$\ln \frac{a_1}{\eta_1} = -\left(\frac{zEF}{RT} + \ln \eta_1\right) + \ln a_2' . . \quad (230)$$

Thus by introducing the activity coefficient as the ratio of the activity to concentration, into equation (230) we obtain the relation :

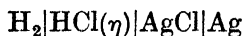
$$\ln f_1 = -\left(\frac{zEF}{RT} + \ln \eta_1\right) + \ln a_2' . . \quad (231)$$

By extrapolating the curve which is obtained by plotting $-\left(\frac{zEF}{RT} + \ln \eta_1\right)$ against η_1 to $\eta_1 = 0$, the value of $\ln a_2'$ is determined at infinite dilution, where $\eta_1 = 0$, $f_1 = 1$, and therefore $\ln f_1 = 0$. The value of the activity coefficient at any other concentration may then be found from the corresponding value of $-\left(\frac{zEF}{RT} + \ln \eta_1\right)$ read off by interpolation from the graph (see Fig. 73).

The method has been extended to other types of cell, and it has been widely employed for determining the activity coefficients of electrolytes both in aqueous and non-aqueous solutions. The investigations on dilute solutions of hydrochloric acid illustrate its value and accuracy.¹

¹ C. A. Linhart, *J. Amer. Chem. Soc.*, **41** (1919), 1175.
G. Scatchard, *ibid.*, **47** (1925), 641.
M. Randall and L. E. Young, *ibid.*, **50** (1928), 989.
H. S. Harned and Ehlers, *ibid.*, **55** (1933), 2179.

For a hydrochloric acid cell,



the E.M.F. is given by :

$$E - E^0 = \frac{2RT}{zF} \ln a$$

where a is the mean activity of the acid. Thus

$$\frac{2RT}{zF} \ln f = - (E - E^0) - \frac{2RT}{zF} \ln \eta \quad . \quad (232)$$

To find the value of E^0 (the standard electrode potential of the silver-silver chloride electrode), an extrapolation may be made using the Debye-Hückel expression for $\ln f$ or better, by using a slightly modified form of the extended Hückel equation ¹ (see Chapter VIII), viz.:

$$\ln f = - a\sqrt{\eta} + b\eta$$

After substituting for the relative constants at 25° C., (232) now becomes :

$$0.1183 \log f_1 = - (E - E_0) - 0.1183 \log \eta_1$$

or

$$0.1183 \log f_1 = E_0 - [E + 0.1183 \log \eta_1] \quad . \quad (233)$$

Using the limiting value 0.2221 for $[E_0 + 0.1183 \log \eta_1]$ which has been obtained by graphical extrapolation (Randall and Scott) it is therefore possible to calculate the activity coefficients, and hence the activities,² since

$$\frac{a_{\pm}}{\eta_1} = f_{\eta} \text{ and } a_1 = a_{\pm}^2$$

In Table IV the best values at 25° C. are given for a wide range of concentrations. It is seen that the activity coefficient decreases from unity at zero concentration, passes

¹ D. I. Hitchcock, *J. Amer. Chem. Soc.*, **50** (1928), 2076.

² The extrapolation is now always carried out using the Debye-Hückel expression for $\ln f$: *e.g.*, Harned and Crawford, *J. Amer. Chem. Soc.*, **59** (1937), 1903. The values quoted above are taken from earlier work on the thermodynamics of hydrogen chloride solutions but they serve to illustrate the method of calculating the activity coefficients from the E.M.F. data. The measurements on hydrogen chloride solutions have been extended to concentrations up to 16*N* by Åkerlöf and Teare, *J. Amer. Chem. Soc.*, **59** (1937), 1855.

through a minimum at about $\eta_1 = 0.762$, and subsequently increases again. This behaviour has been observed for many other strong electrolytes (see Chapter IX).

TABLE IV

Activities and Activity Coefficients of Aqueous Hydrochloric Acid Solutions at 25° C.

η_1	f_{η_1}	$a_{\pm}$	a_1	η	f_{η_1}	$a_{\pm}$	a_1
0.0005	0.965	0.000493	0.000000234	0.2	0.793	0.1527	0.0234
0.001	0.959	0.000960	0.000000865	0.3	0.749	0.225	0.0504
0.002	0.946	0.001893	0.00000358	0.4	0.744	0.293	0.0883
0.005	0.923	0.004625	0.0000217	0.5	0.743	0.3715	0.138
0.01	0.901	0.00901	0.0000813	0.6	0.751	0.450	0.202
0.02	0.872	0.01741	0.000304	0.75	0.768	0.576	0.331
0.05	0.839	0.0419	0.00176	1.0	0.802	0.781	0.643
0.1	0.794	0.0793	0.00632	2.0	0.997	1.960	3.96

(d) *Determinations of Activities from Freezing-point Measurements.*¹

The calculation of the activities and activity coefficients from freezing-point measurements has certain advantages compared with the other methods which have been described. The measurements are subject to only a small experimental error, and they do not involve any side reactions such as may occur in the E.M.F. measurements, by the solution of electrode material. The calculations are, however, very laborious and, for all but the lowest concentrations, have been worked out in only a very few cases.²

It is always necessary in the calculations to know the variation of the activity with the temperature. From equation (177)

$$\Delta \bar{F} = \bar{F}_2 - \bar{F}^0 = RT \ln a_2$$

for an isothermal transfer of the component II from the standard state to the state in which its activity is a_2 . If the change in partial molar heat content during this process be $\Delta \bar{H}$, we have, from (159):

$$\frac{\partial}{\partial T} \left(\frac{\Delta \bar{F}}{T} \right) = \frac{\Delta \bar{H}}{T^2} \quad . \quad . \quad . \quad (234)$$

¹ M. Randall and C. R. Fairley, *Chem. Rev.*, **4** (1927), 291.

² T. F. Young, *ibid.*, **13** (1933), 103.

Combining (234) and (177)

$$\frac{\partial \ln a_2}{\partial T} = - \frac{\Delta \bar{H}}{RT^2} \quad . \quad . \quad . \quad (235)$$

we have the required variation of the activity with temperature. In equation (235) $\Delta \bar{H}$ is not, however, constant, but, from Kirchoff's equation, if $(C_p)_2$ and $(C_p)_0$ denote the heat capacities in the given and in the standard states,

$$\frac{\partial \Delta \bar{H}}{\partial T} = (C_p)_2 - (C_p)_0 \quad . \quad . \quad . \quad (236)$$

The heat capacities themselves change with temperature and these variations may be expressed by empirical equations of the type

$$C_p = a + bT + cT^2 + dT^3 \quad . \quad . \quad (237)$$

and a direct integration of (236) is therefore possible only over a small range of temperature.

Equation (235) is modified by Lewis¹ for calculations in the neighbourhood of the freezing point by substituting

$$T = \Theta - \theta \quad . \quad . \quad . \quad (238)$$

where Θ is the freezing point and T is the temperature used, θ degrees below the freezing point. When the relevant quantities are then introduced in the expanded equation obtained from (235), (236) and (237) for the change

$$H_2O_{\text{liquid}} = H_2O_{\text{solid}}$$

Lewis finds that

$$\partial \ln a_s = (-0.009696 - 0.0000103 \theta) \partial \theta \quad . \quad (239)$$

In these equations θ is, of course, the lowering of the freezing point and by convention the activity of the ice a_s is equal to the activity of the water a_1 in the solution at the freezing point. (239) therefore becomes :

$$\partial \ln a_1 = (-0.009696 - 0.0000103 \theta) \partial \theta \quad . \quad (240)$$

Now, provided θ , the depression of the freezing point, is regarded as a property of the solution only, a_1 may be supposed, at a given concentration, to be independent of the

¹ Lewis and Randall, "Thermodynamics," 1923, Chapter XXIII, pp. 282 *et seq.*

temperature. Thus from (220) by substituting in the value of $\partial \ln a_1$ in (240), we have :

$$\partial \ln a_2 = -\frac{\eta_1}{\eta_2} (-0.009696 - 0.0000103 \theta) \partial \theta \quad (241)$$

But for pure water with a molecular weight of 18.02, η_1 may be replaced by $\frac{1000}{18.02} = 55.51$. Equation (241) therefore becomes :

$$\partial \ln a_2 = -\frac{55.51}{m} (-0.009696 - 0.0000103 \theta) \partial \theta \quad (242)$$

where m is the concentration now in grams per litre. Provided the solutions are dilute—i.e., that θ approaches zero— a_2 may be replaced by m , i.e. :

$$\partial \ln m = \frac{55.51 \times 0.009696}{m} \partial \theta \quad (243)$$

for the last term in equation (242) will be quite negligible compared with the first term. From (243)

$$\frac{\partial \theta}{\partial m} = 1.858 \quad (244)$$

Lewis replaces this number 1.858, which is characteristic for aqueous solutions and is the molecular lowering of the freezing point at infinite dilution, by the symbol λ , so that (242) becomes :

$$\partial \ln a_2 = \frac{\partial \theta}{\lambda m} + 0.00057 \frac{\theta \partial \theta}{m} \quad (245)$$

In order to determine the activity at the freezing point, it is now necessary to integrate equation (245). As the equation stands, integration would be difficult, since in dilute solutions where a_2 is small, $\ln a_2$ is a large negative quantity. The process of integration may, however, be simplified by making the simple transformation

$$j = 1 - \frac{\theta}{\lambda m} \quad (246)$$

By differentiation

$$\frac{\partial \theta}{\lambda} = \partial m - m \partial j - j \partial m \quad (247)$$

Now, in equation (245) the second term is never appreciable until high concentrations are reached, and (246) and (247) may therefore be substituted in the equation

$$\partial \ln a_2 = \frac{\partial \theta}{\lambda m} \quad . \quad . \quad . \quad . \quad . \quad (248)$$

$$\text{giving} \quad \partial \ln a_2 = \frac{\partial m}{m} - \partial j - j \frac{\partial m}{m} \quad . \quad . \quad (249)$$

$$\text{or} \quad \partial \ln a_2 = \partial \ln m(1 - j) - \partial j \quad . \quad . \quad (250)$$

$$\text{i.e.} \quad \partial \ln \frac{a_2}{m} = j \partial \ln m - dj \quad . \quad . \quad . \quad (251)$$

In this equation each term becomes zero at infinite dilution, so that (251) is in a convenient integrable form :

$$\left. \begin{aligned} \ln \frac{a_2}{m} &= - \int_0^m j \frac{\partial m}{m} - j \\ \text{or} \quad \ln \frac{a_2}{m} &= - \int_0^m j \partial \ln m - j \end{aligned} \right\} \quad . \quad . \quad (252)$$

Although it may not be possible to integrate this equation analytically in every case, the integral represents the area under the curve obtained by plotting $-j/m$ against m . If the second term in (245) is counted in, after making the j transformation, (252) now becomes :

$$\ln \frac{a_2}{m} = - \int_0^m j \partial \ln m - j + \int_0^m 0.00057 \frac{\theta}{m} \cdot \partial \theta \quad . \quad (253)$$

and the second integral is the area under the graph obtained by plotting $0.00057 \theta/m$ against θ .

Calculations made from equation (253) neglect the heat of dilution, but if this is taken into account, extra terms must be included, while the data available rarely warrant such a detailed theoretical consideration except at high concentrations. The freezing-point method for determining activity coefficients is possibly the most accurate, although until recently it has not been used so widely as the E.M.F. method, due to the scarcity of accurate experimental data.¹ It is, however, important to realise that, while the freezing-

¹ Adams, *J. Amer. Chem. Soc.*, **37** (1915), 481.

Hovorka and Rodebush, *ibid.*, **47** (1925), 1614.

Randall and Vanselow, *ibid.*, **46** (1924), 2433.

Scatchard, Jones and Prentice, *ibid.*, **54** (1932), 2676.

point method is perfectly general and may be applied to any substance in solution, electrolyte or non-electrolyte, the E.M.F. method is limited by the necessity of finding suitable electrodes. Some interesting evidence is available from measurements made on dilute solutions of sulphuric acid solutions for the mutual confirmation of results obtained using the vapour-pressure, the E.M.F., and the freezing-point methods.¹ The measurements have been carried out over a very wide range of concentration from infinite dilution to 8M and, as shown by the curves in Fig. 52, the agree-

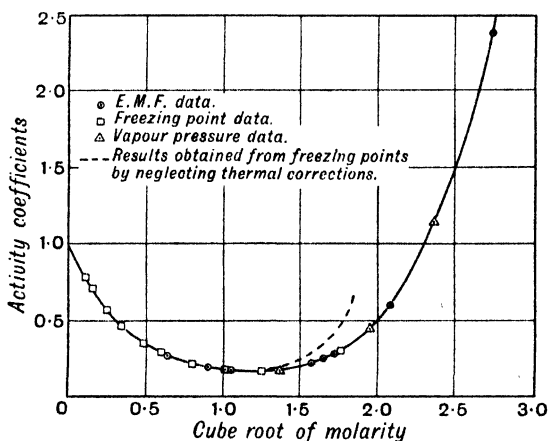


FIG. 52.—ACTIVITY COEFFICIENT MEASUREMENTS OF H_2SO_4 BY DIFFERENT METHODS.

ment between the results by the three different methods is surprisingly good, and justifies the employment of the thermal corrections made in calculating the activity coefficients from freezing-point data. The broken line represents the curve which would have been obtained for the variation of the activity coefficient with the molarity had no account been taken of the thermal corrections.

Activities in Mixtures of Strong Electrolytes.

Measurements of the activities of strong electrolytes have been extended to mixtures² where the two methods which

¹ Lewis and Randall, *J. Amer. Chem. Soc.*, **43** (1921), 142.

² H. S. Harned, "Electrochemistry of Solutions"; "Physical Chemistry," ed. H. S. Taylor, New York, 1930, Vol. I, p. 820.

have been most widely used are those which determine the function from solubility measurements of one electrolyte in the presence of others ¹ and by E.M.F. measurements of cells containing one electrolyte to which are added various amounts of the second electrolyte containing a common ion.² Measurements by these methods have shown that "in any dilute solution the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength."³

In stronger solutions of mixtures of electrolytes the activity of one electrolyte depends in a specific way on the nature of the other ions present. From an extended series of measurements on the partial molar free energy of hydrochloric acid in the presence of chlorides ⁴ it has been demonstrated

(a) that for a constant total electrolyte concentration the activity of the hydrogen chloride is linearly proportional to its molar fraction;

(b) that for a constant acid concentration and a variable salt concentration, the activity coefficients of the hydrogen chloride vary with the square root of the ionic strength exactly as if the behaviour of only a single electrolyte was being observed.

These facts have received a very satisfactory explanation in terms of the theory to be outlined in the next chapter (see also Chapter IX).

¹ A. A. Noyes and collaborators, *J. Amer. Chem. Soc.*, **33** (1911).
J. N. Brönsted, *ibid.*, **42** (1920), 761.

² H. S. Harned, *ibid.*, **38** (1916), 1984.

³ The expression "in dilute solutions" is used in the same sense as used by Lewis to infer that the statement is valid, strictly speaking, only when the dilution is indefinitely increased—the concentration at which the statement may no longer be regarded as a valuable generalisation will depend upon the limits of error within which the relevant measurements may be made.

⁴ Harned and Åkerlöf, *Physikal. Z.*, **27** (1926), 411, and numerous other papers by Harned and his collaborators, in *J. Amer. Chem. Soc.*

CHAPTER VII

THE THERMODYNAMIC PROPERTIES OF STRONG ELECTROLYTES

Milner's Theory.

DUE to the formation of ion atmospheres round the ions of an electrolyte, the thermodynamic properties of a solution of this will not be the same as those for a solution of a non-electrolyte of the same strength. This change of properties in an electrolyte will depend on the different value which the free energy has in an assembly of charged particles like an electrolytic solution. Once the value of this free energy has been determined, therefore, all the thermodynamic functions of the solution can be calculated. Milner was the first to recognise clearly that the anomaly between the thermodynamic properties of electrolytes calculated by the gas laws, and the experimentally observed values, was due to interionic electrostatic forces.¹ He rejected the Arrhenius view that the small fractions of undissociated molecules in the solutions of strong electrolytes would account for the observed deviations, on the ground that this theory gives results for the variation of conductivity with concentration which are entirely at variance with the mass-action law. Milner assumed that the modified Clausius virial equation, (183)

$$PV = \frac{1}{3}nmc^2 + \frac{1}{2}\Sigma r[\phi(r)]$$

could be applied to solutions of strong electrolytes. In this equation a term is added to the ordinary gas equation, which attempts to take account of the combination of the intermolecular forces to the total energy of the gas. In the case

¹ S. R. Milner, *Phil. Mag.*, **25** (vi) (1913), 742. For a critical review of the historical development of the interionic attraction theory, refer to G. Scatchard, *Chem. Rev.*, **13** (1933), 7.

of solutions, of course, the pressure P would be osmotic pressure and the nature of the term $\Sigma r[\phi(r)]$ could be determined for an assemblage of ions, from a knowledge of the interionic forces. The electrolyte solution was therefore supposed to have a finite virial which, when calculated from the known laws of interionic attraction, could be applied by ordinary thermodynamic methods to determine the osmotic properties of electrolytes.¹ The calculations were made by strict statistical reasoning, but they gave results which are difficult to verify experimentally.

The Theory of Debye and Hückel. First Approximation.

In 1923, Debye and Hückel solved the problem for dilute solutions, in a different manner.² In a solution of a completely dissociated electrolyte there is not a random distribution of the ions. Due to the Coulomb forces between the ions, there is always a greater probability of finding an ion of the opposite charge near a given ion than of finding one of the same charge at the same distance. In consequence of this, each ion is accompanied by an atmosphere of other ions the net charge of which is equal and opposite to that of the central ion. The calculation of the free energy of an electrolyte, in order to allow for the effect of the ion atmosphere, requires therefore a specific knowledge of the distribution of charge—i.e., of the distribution functions inside this ion atmosphere.

In the most general case we can calculate the form of these distribution functions when the only forces acting are interionic. They may be shown³ to be of the form

$$\bar{f}_{ij} = n_i n_j \left(1 - \frac{e_j \bar{\psi}_i}{kT} \right) \quad . \quad . \quad . \quad (254)$$

where $n_i n_j$ are the concentrations of the ions of types i and j , e_j is the charge on ions of type j , $\bar{\psi}_i$ is the electric potential due to the ion atmosphere round an ion i , and $\bar{f}_{ij}$ is the distribution function or probability density of ions of the type

¹ S. R. Milner, *Phil. Mag.*, **23** (vii) (1912), 551.

² Debye and Hückel, *Physikal. Z.*, **24** (1923), 185.

³ Onsager, *ibid.*, **28** (1937), 277, § 5.

Falkehaugen, "Electrolytes," Oxford (1933), p. 182.

j in the atmosphere of an ion of type i . In the derivation of the free energy expression of a simple binary electrolyte, however, the calculations may be made more simply by the following argument. In a volume dv of solution at a small distance r from a positive ion, the charge of which is ze (z = valency and e = the electronic charge), there will be a net negative charge in the elemental volume due to the ion atmosphere having, on the whole, a charge opposite to that of the central ion.¹ If N be the number of particles per unit

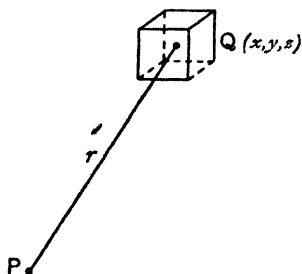


FIG. 53.

volume, N_+ the number of positive ions, and N_- the number of negative ions at a point P within the volume dv and $\bar{\psi}$ the mean potential at P , then the work done in bringing a positive ion from infinity to P is $+ze\bar{\psi}$, where ze is the numerical value of the charge on the ion. According to the Boltzmann principle, the ionic distribution of negative ions in

the volume dv depends on the exponential of the ratio of potential energy to kT , and similarly for positive ions. Thus

$$\left. \begin{aligned} N_+ &= N_0 \exp. \left(-\frac{ze\bar{\psi}}{kT} \right) \\ N_- &= N_0 \exp. \left(+\frac{ze\bar{\psi}}{kT} \right) \end{aligned} \right\} \quad (255)$$

and since $ze\bar{\psi}$ is always much smaller than kT for all ordinary conditions, $\exp. \left(-\frac{ze\bar{\psi}}{kT} \right)$ is a little less than unity and

$$\exp. \left(+\frac{ze\bar{\psi}}{kT} \right) = 1 / \exp. \left(-\frac{ze\bar{\psi}}{kT} \right)$$

is a little greater than unity. The application of the Boltzmann theorem gives therefore a result agreeing with the

¹ This assumes that the time interval over which the change in the ion atmosphere is averaged is large compared with the frequency with which the ions move under thermal agitation.

fundamental assumption that the excess of negative over positive ions in the ion atmosphere of a positive ion is only very small. The average electric charge density in the elemental volume is therefore

$$\rho = zeN_0 \left[\exp. \left(-\frac{ze\bar{\psi}}{kT} \right) - \exp. \left(+\frac{ze\bar{\psi}}{kT} \right) \right] \quad (255)$$

and if $ze\bar{\psi}$ is very small, as becomes the case in very dilute solutions where r increases, we may write (255) as

$$\rho \approx zeN_0 \left(1 - \frac{ze\bar{\psi}}{kT} - 1 - \frac{ze\bar{\psi}}{kT} \right) = -\frac{2z^2e^2N_0\bar{\psi}}{kT} \quad (256)$$

Now if we wish to eliminate ρ , we must have another equation between ρ and the mean potential $\bar{\psi}$ at an ion due to its ion atmosphere. Following Debye and Hückel we therefore use an equation due to Poisson,¹ which relates these quantities, viz :

$$4\pi\rho = -\nabla^2\bar{\psi} \quad . \quad . \quad . \quad (257)$$

where ∇^2 denotes Laplace's operator

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

For the electric density in the ion atmosphere, where D is the dielectric constant of the solution, Poisson's equation (256) becomes :

$$\frac{4\pi\rho}{D} = -\nabla^2\bar{\psi} \quad . \quad . \quad . \quad (258)$$

Now, the potential round an ion due to the ion atmosphere is more conveniently considered in polars, and the Laplacian operator may be transformed to polars by the following equation :

¹ A simple proof of this theorem is available using vector analysis, for if ρ be the volume density of distribution of electric charge at all points of a homogeneous conductor, the flux outwards through a small volume $\mathfrak{V}$ surrounding any point is $4\pi\rho\mathfrak{V}$. Thus by the theorem of flux

$$\begin{aligned} \mathfrak{V} \operatorname{div} \bar{Q} &= 4\pi\rho\mathfrak{V} \\ \operatorname{div} \bar{Q} &= 4\pi\rho = + \operatorname{div} (\operatorname{grad} \bar{\psi}) \end{aligned}$$

i.e., in cartesian

$$4\pi\rho = -\bar{\nabla}^2\bar{\psi}.$$

$$-\frac{4\pi\rho}{D} = \nabla^2\psi = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \quad (259)$$

As there is no reason but to suppose that the potential ψ is spherically symmetrical about the central ion, we may write :

$$\frac{\partial^2 \psi}{\partial \phi^2} = \frac{\partial \psi}{\partial \theta} = 0 \quad . \quad . \quad . \quad (260)$$

and therefore from (259) and (256)

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) = \frac{8\pi z^2 e^2 N_0 \psi}{DkT} = \kappa^2 \psi \quad . \quad . \quad (261)$$

Here the equation has been simplified by putting

$$\kappa = \sqrt{\frac{8\pi e^2 z^2 N_0}{DkT}} \quad . \quad . \quad . \quad (262)$$

so that κ is therefore proportional to the square root of the concentration. The general solution to equation (261) is

$$\psi = \frac{Ae^{-\kappa r}}{r} + \frac{A'e^{\kappa r}}{r} \quad . \quad . \quad . \quad (263)$$

according to which, as r increases, the mean potential tends to infinity. To satisfy the known boundary condition that $\psi = 0$ when $r = \infty$, it follows that $A' = 0$. For dilute solutions r is always greater compared with the ionic radius, and it is a sufficient approximation to consider the ion as a point charge ze due to which the potential at a distance r is

$$\psi = \frac{ze}{Dr} \quad . \quad . \quad . \quad (264)$$

Thus for very small values of r the potential will, to an increasing extent, be due to both the central ion and the ion atmosphere. Thus the increment of the ion atmosphere becomes negligible, and we may write from equation (264) :

$$\psi = \frac{ze}{Dr} = \frac{A}{r} \quad . \quad . \quad . \quad (265)$$

$$\text{i.e.,} \quad A = \frac{ze}{D} \quad . \quad . \quad . \quad (266)$$

The expression

$$\mu = \frac{1}{2} \sum_i n_i z_i^2 \quad . \quad . \quad . \quad (273)$$

is defined by Lewis as the ionic strength of the solution. Hence from (272), μ and κ are related by the equation

$$\frac{1}{\kappa} = K \sqrt{\frac{DT}{\mu}} \quad . \quad . \quad . \quad (274)$$

where K is a constant independent of the particular solution. For uni-univalent electrolytes in aqueous solution at a molecular concentration of 0.001, $1/\kappa$ is of the order 10^{-6} cm. The thickness of the ion atmosphere is obviously inversely proportional to the root of the concentration, since κ is proportional to the root of the concentration.

The difference in free energy of a solution of an electrolyte which behaves ideally at a concentration c_2 and a solution of the same electrolyte at a very low concentration c_1 is given by :

$$\int_{c_1}^{c_2} P dv = -F \quad . \quad . \quad . \quad (275)$$

If, now, the charges on the ions are supposed to be removed infinitely slowly, the solution may then be considered perfect and the process of concentration from c_1 to c_2 may be carried out in the usual reversible manner, using a semi-permeable membrane as a piston. The total work in this process is :

$$\int_{c_1}^{c_2} P_{id} dv = -F_{id} = \int_{v_\infty}^v P_{id} V \quad . \quad . \quad (276)$$

and the electrical work Fe_1 done in removing and restoring the charges to the ions is equal to $F - F_{id}$. The work of discharge of all the ions at v_∞ (infinite dilution) is found from the work done in charging a sphere of radius r in a medium of dielectric constant D to a charge e , which is equal to $\frac{e^2}{2Dr}$. Considering the ion as spherical, the work of discharge in infinitely dilute solution in a solvent of dielectric constant D is therefore :

$$W_d = -\frac{e^2}{2Dr} \quad . \quad . \quad . \quad (277)$$

When the ions are re-charged at a finite concentration v , the work done will consist of two parts, since an ion atmosphere is set up. The one part, by analogy with W_d , is $\frac{e^2}{2Dr}$, where D is the dielectric constant of the solution and the other is a factor arising from the Coulomb forces. This second term is taken as equal to the work done in discharging the potential due to the ion atmosphere. During this discharge the charge on the central ion may be supposed to be some fraction of e equal to λe , and the work of discharge is then

$$e \int_{\lambda=0}^{\lambda=1} \bar{\psi}_{II\lambda} d\lambda \quad . \quad . \quad . \quad (278)$$

where $\bar{\psi}_{II\lambda}$ is the potential due to the ion atmosphere at the moment considered. Since also

$$\psi_{II\lambda} = \lambda^2 \bar{\psi}_{II} \quad . \quad . \quad . \quad (279)$$

we have, by substituting from (277)

$$e \bar{\psi}_{II} \int_{\lambda=0}^{\lambda=1} \lambda^2 d\lambda = \frac{\bar{\psi}_{II} e}{3} \quad . \quad . \quad . \quad (280)$$

and the total electrical work is given by :

$$- \frac{e^2}{2Dr} + \frac{e^2}{2D_1 r} + \bar{\psi}_{II} \frac{e}{3} = - \frac{e^2 r}{3D} \quad . \quad . \quad (281)$$

for, in the very dilute solutions the numerical values of D and D_1 may be supposed equal. The total electrical work per c.c., which is equal to the free energy of the solution, is then :

$$F_{el.} = - \sum_i \frac{N_0 e^2 z^2 \kappa}{3D} \quad . \quad . \quad . \quad (282)$$

the summation now being taken over all the particles in the solution. Since also from (272)

$$\kappa^2 = \sum_i \frac{4\pi e^2 z^2}{DkT} \cdot N_0$$

then for a volume V of the solution, $F_{el.}$ in (282) has the value

$$F_{el.} = - \sum_i V \frac{N_0 e^2 z^2 \kappa^2}{3D} \cdot \frac{DkT}{4\pi N_0 e^2 z^2} = - \sum_i \frac{kT \kappa^3 V}{12\pi} \quad . \quad (283)$$

From the value of the electric free energy of the solution given in Debye and Hückel's first analysis by equation (283), we

are able to calculate the various thermodynamic coefficients of a dilute solution of a strong electrolyte and to compare these with experimentally determined values for a verification of the theory.

The Osmotic Coefficient.

If in equation (283) we write :

$$\kappa = \frac{\kappa'}{\sqrt{v}} \quad . \quad . \quad . \quad . \quad . \quad (284)$$

so that κ' may be treated as independent of v , the new value so obtained for the free energy gives, when differentiated with respect to v ,

$$\left(\frac{\partial F_{\text{el}}}{\partial v}\right)_T = \sum_i \frac{kT\kappa'^3}{24\pi} \cdot \frac{1}{v^{\frac{3}{2}}} = \sum_i \frac{kT\kappa^3}{24\pi} \quad . \quad . \quad (285)$$

Also from the definition of free energy (equation 145),

$$\left(\frac{\partial F_{\text{el}}}{\partial v}\right)_T = P_{\text{el}}$$

$$\text{i.e.} \quad P_{\text{actual}} = P_{\text{ideal}} - P_{\text{el}} = P_{\text{ideal}} - \left(\frac{\partial F_{\text{el}}}{\partial v}\right)_T \quad . \quad (286)$$

Now the osmotic coefficient g_0 is defined by the equations

$$\left. \begin{aligned} g_0 &= \frac{\text{observed osmotic pressure}}{\text{calculated osmotic pressure}} = \frac{P_{\text{actual}}}{P_{\text{ideal}}} \\ g_0 &= \frac{\text{observed f.p. depression}}{\text{calculated f.p. depression}} \end{aligned} \right\} \quad . \quad (287)$$

$$\text{i.e., from (286)} \quad g_0 = \frac{P_{\text{ideal}} - P_{\text{el.}}}{P_{\text{ideal}}} \quad . \quad . \quad . \quad . \quad (288)$$

Thus from (285), (286), and (288) we have :

$$1 - g_0 = \left(\frac{\partial F_{\text{el}}}{\partial v}\right) / P_{\text{id.}} = \frac{\sum_i kT\kappa^3}{24\pi P_{\text{id.}}}$$

Also for a perfect solution

$$P_{\text{id.}} = \sum_i n_i kTN$$

so that

$$1 - g_0 = \sum_i \frac{\kappa^3}{24\pi N n_i} \quad . \quad . \quad . \quad (289)$$

If we substitute into (289) the value of κ from (272), replace D_0 the dielectric constant of water at 0° by its value 88.2, put $T = 273$ and write :

$$\zeta = (\sum_i \nu_i z_i^2)^{\frac{1}{2}}$$

where ν_i is the number of ions of type i formed by the dissociation of one molecule of the salt, the equation for g_0 becomes

$$1 - g_0 = 0.263 \zeta \sqrt{\text{concentration}} \quad . \quad (290)$$

for aqueous solutions at 0° . It is seen, therefore, that, by assuming the formation of ion atmospheres due to the electrostatic forces round the ions, the calculated osmotic coefficient depends in a very specific manner upon the charges of the ions (as included in the factor ζ) and, like the other properties, of strong electrolytes, is proportional to the square root of the concentration.

Experimental Determinations of the Osmotic Coefficients.

Equation (290) may be tested from a variety of determinations of the osmotic coefficient, but only the osmotic pressures and the lowering of the freezing points can be determined with sufficient accuracy in the very dilute solutions to which the theory applies, to make a comparison of the theory with experimental results reliable.¹ The fact that the osmotic pressures of even very dilute solutions are relatively quite large compared with the lowering of the freezing points of the same solutions makes it evident that, if the experimental difficulties could be surmounted, the method of direct osmotic-pressure determination should give values for the osmotic coefficient on which more reliance could be placed than on results from the difficult determinations of the very small freezing-point depressions. On account of the

¹ Just as there are rational and practical activity coefficients according to the concentration scale chosen (see p. 163), so also there are rational and practical osmotic coefficients. Most experimental results express the coefficients in terms of molalities—i.e., as practical coefficients—but in the very dilute solution range the differences between the practical and rational coefficients rarely exceed the experimental error (Guggenheim, *Phil. Mag.*, 19 (vii) (1935), 588).

difficulty of obtaining membranes which are completely permeable to ions, the ordinary methods of osmotic pressure determination are applicable only to non-electrolytes. The difficulty has, however, been overcome by using the vapour of the solvent separating the solvent and the solution as a

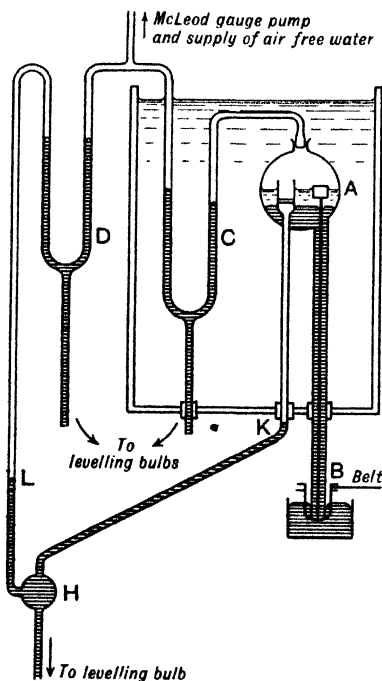


FIG. 54.—DETERMINATION OF OSMOTIC PRESSURE (Townend).

membrane, through which distillation of the solvent only can take place.¹ By applying to the solution a tension equal and opposite to its osmotic pressure, the vapour pressures over the pure solvent and the solution will be equal, and no distillation will take place in either direction. In the experimental arrangements which adopt this principle (see Fig. 54), the solvent is situated so that the surface of separation between solvent and vapour consists of a large number of very fine capillary surfaces obtained by terminating the solvent in a fine grain porous plate. By supporting the column of solution on a mercury column connected with a levelling bulb,

the tension on the solution and the curvatures of the capillary surfaces may be varied, and therefore the vapour pressure above the solution, may be altered. Positive and negative rates of distillation from the plate to the solution for different applied tensions may then be measured, and the tension for a zero rate of distillation—i.e., the osmotic pressure of the solution—may be determined by interpolation.² (Fig. 55).

¹ R. V. Townend, *J. Amer. Chem. Soc.*, **50** (1928), 2958.

² F. T. Martin and L. H. Shultze, *J. Physical Chem.*, **35** (1931), 638.

The osmotic pressures of dilute solutions are extremely sensitive to small changes in temperature, and it is very necessary to avoid fluctuations in the temperature of the thermostat of more than 0.0005°C. when measurements are being made on solutions of concentrations about 0.001M. Unfortunately, no measurements of the osmotic pressures of dilute aqueous solutions of Debye-Hückel electrolytes have yet been undertaken with a sufficient accuracy of temperature control to enable a comparison of theory and experiment to be made. But with modern methods of temperature control there is no reason why the direct determinations of the osmotic coefficient from osmotic pressures should not

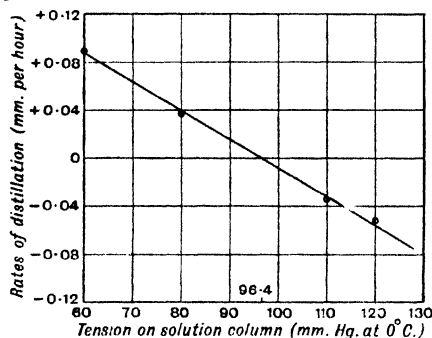


FIG. 55.—INTERPOLATION OF OSMOTIC PRESSURE READINGS.

provide one of the most accurate methods of verifying the predictions of the Debye-Hückel theory.¹

Of the other indirect methods for determining the osmotic coefficient, only its determination from measurements of the lowering of the freezing point is capable of anything like the accuracy necessary to provide an adequate confirmation of the limiting law for this function. The first marked advance on Raoult's method for determining freezing points by supercooling a solution of known concentration and recording the highest temperature reached, was made by Roloff and Richards.² They mixed the salt solutions

¹ Some measurements of a high order of accuracy have been undertaken by W. C. Echelberger on non-aqueous solutions of electrolytes, *J. Amer. Chem. Soc.*, **53** (1931), 2025.

² Roloff and Richards, *Z. physikal. Chem.*, **18** (1895), 572; *ibid.*, **44** (1903), 563.

directly with separately frozen pure ice, and showed that the equilibrium concerned in the freezing of solutions was then quickly established. For measurements of the highest accuracy, however, unbalanced external influences such as may arise, for example, from stirring the solution, must be eliminated by a differential method. The freezing-point depression may then be accurately measured by a multiple thermocouple situated between the two liquids.¹ For measurements of sufficient accuracy to verify the Debye-

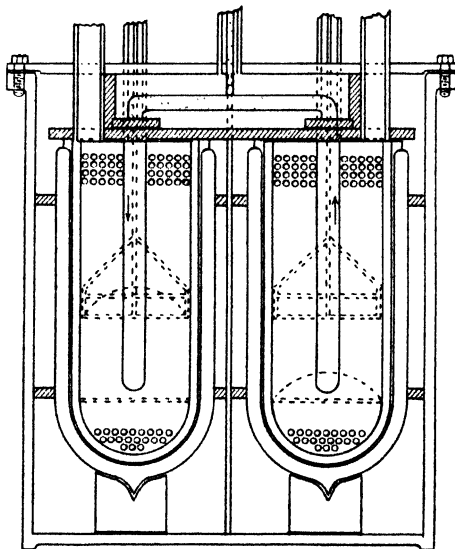


FIG. 56.—DIFFERENTIAL FREEZING-POINT APPARATUS (Scatchard).

Hückel theory in very dilute solutions, however, a number of important practical precautions have to be observed even in the operation of the differential method.² Circulation of the liquids in the freezing vessels (Dewar vessels) must be ensured by dividing each vessel into three compartments by parallel vanes, the outer two compartments being used as pump cylinders which circulate the liquid at each up-stroke into the inner compartment containing the ice (see Fig 56).

¹ L. H. Adams, *J. Amer. Chem. Soc.*, **37** (1915), 481.

Hovorka and Rodebush, *ibid.*, **47** (1925), 1614.

Randall and Vanselow, *ibid.*, **46** (1924), 2418.

² See G. Scatchard, P. T. Jones, and S. S. Prentice, *J. Amer. Chem. Soc.*, **54** (1932), 2676.

The copper-constantan thermocouples, which have very large temperature coefficients of E.M.F., used for measuring the difference in the equilibrium temperatures, are arranged on a Π -shaped frame, the two limbs passing into the middle compartments of each vessel. With very dilute solutions, the accuracy with which the analysis of the equilibrium mixtures is possible also determines to a large extent the accuracy of the method and it is probable that interferometer measurements of the concentration are more accurate than determinations made from observations of the electrical conductivity, for in the latter case the uncertain errors due to the solvent correction become more important the more dilute the solution.

Unfortunately it is a disadvantage of all methods of verifying the Debye-Hückel predictions that, as the solutions become more dilute so that the theoretical equations can be applied with greater confidence, uncontrollable experimental errors become of increasing importance, and the same confidence cannot be placed in the experimental results. It is therefore only possible to show that the observed values would approach the limiting law if all the experimental errors were eliminated and if the measurements could be made at the very lowest concentrations. The very marked influence of the valency of the ions and of the dielectric constant of the medium on the values of the osmotic coefficients should therefore easily be capable of experimental verification. On the other hand, the actual limiting slopes can never be experimentally determined with the highest degree of accuracy, due to the impossibility of making an accurate extrapolation from the region of experimental observations to infinite dilution. Some of the results which have been obtained by the differential freezing-point method for the osmotic coefficient are compared with the predicted limiting slopes in the diagram (Fig. 57). The shift of the curve for a change in the valency type of the salt is very marked, and the general effect of decreasing the dielectric constant of the solvent from water to the alcohols, resulting in an increase in the slopes of the curves, has also been found experimentally.¹

¹ O. F. Frivold, *J. Physical Chem.*, **30** (1926), 1153.

Even, however, at the lowest concentrations of uni-univalent salts where measurements have been made with accuracy, there is a considerable difference between the predicted limiting slopes and those obtained by an approximate extrapolation of the observed curves to infinite dilution. It must be concluded, therefore, that a complete verification of the predictions of the interionic attraction theory cannot be made at present from measurements of the simple osmotic

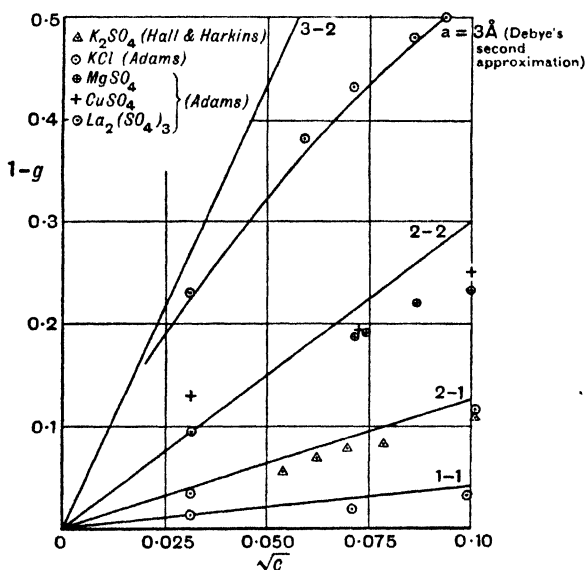


FIG. 57.—OSMOTIC COEFFICIENTS OF SOME VALENCY TYPES OF ELECTROLYTES.

properties of solutions,¹ and we must investigate other thermodynamic properties of the solution which can be interpreted by the theory.

The Activity Coefficient.

An expression for the activity coefficient of a dilute solution of a strong electrolyte may be developed from the potential

¹ It should be noted, however, that at least one attempt has been made (Scatchard, *Chem. Rev.*, **19** (1936), 309) to interpret the observed experimental data by extending the theory of interionic attraction to more concentrated solutions, where the experimental values of the osmotic coefficients are much more trustworthy.

due to the ion atmosphere ¹ which for a particular ion of the i th species, associated with the valency z_i , is given by (269).

$$\psi_{ii} = - \frac{e\kappa z_i}{D}$$

Now, this is approximately equal to the potential due to the atmosphere at the central ion where the charge is ez_i . Hence the total energy required to remove the ion atmosphere from this ion, is $-e^3\kappa z_i^2/D$ and this is equal to the potential energy of the ion with respect to its atmosphere. The electrical work necessary to transfer an ion from the given solution to infinite dilution is equal to the energy required to discharge the ion in the given solution, less the energy required to charge it in an infinitely dilute solution. This in turn is equal to the work required in order to remove the ion atmosphere all in one stage, followed by subsequently reforming this at infinite dilution, *i.e.*

potential energy of the solution

$$= U_{\text{el.}} = - \sum_i \frac{n_i e^2 z_i^2 \kappa}{2D} \quad . \quad . \quad . \quad (291)$$

If this expression for the potential energy of the solution be compared with the total electrical free energy of the solution per c.c., which is from (282),

$$F_{\text{el.}} = - \sum_i \frac{n_i e^2 z_i^2 \kappa}{3D}$$

it is evident that

$$F_{\text{el.}} = \frac{2}{3} U_{\text{el.}} \quad . \quad . \quad . \quad (292)$$

and the electrical free energy of the solution at constant volume is therefore always a definite fraction of the potential energy of the solution at all temperatures. This relation is quite independent of the temperature variation of the dielectric constant. The value for the electrical free energy of the solution may therefore always be calculated, and the difference between the two expressions (282) and (291) is due to the fact that the electrical free energy has been computed on the supposition that the distribution of charge on the ions

¹ P. Debye, *Physikal. Z.*, **25** (1924), 97.

A. A. Noyes, *J. Amer. Chem. Soc.*, **46** (1924), 1080.

changes continuously from $z_i e$ to zero during the discharging process and is at any instant $\lambda z_i e$. It therefore represents the energy given out when the solution is diluted in the ordinary manner. The potential energy of the solution, on the other hand, represents the work done when the charges on the ions are supposed to be removed all in one stage, and the dilution then carried out on the uncharged ions, followed by the restoration of the charges at infinite dilution.

The expression (282) for the total free energy may be deduced by Milner's method from the Clausius virial equation (183) in which the additional term is equal to the potential of the ions.¹ Debye and Hückel's expression for $U_{el.}$ was calculated by a different method from that adopted by Milner, but using their value for this we can follow the principle of Milner's calculations. For from (183) we have

$$PV = kT + 2U_{el.} \quad . \quad . \quad . \quad (293)$$

where the term $2U_{el.}$ is the energy increase attending the infinite dilution at a temperature T of a solution containing 1 gram-mole of positive and 1 gram-mole of negative ions each of valency z_i at the concentration n_i . Hence from (292)

$$P = 2\sum_i n_i kTc - 2\sum_i \frac{n_i z_i e^2 \kappa}{2D} \quad . \quad . \quad (294)$$

or
$$dP = 2\sum_i n_i RTdc - 2\sum_i \frac{n_i e^2 z_i^2 \kappa}{2D} \quad . \quad . \quad (295)$$

and since
$$-2F = \int_{P_0}^{P_1} \frac{dP}{n_i} \quad . \quad . \quad . \quad . \quad (296)$$

we have from (295)

$$-2F = 2\sum_i n_i \kappa T \ln \frac{c_0}{c_1} - \sum_i \frac{n_i e^2 z_i^2 \kappa}{D} \quad . \quad . \quad (297)$$

This equation for the total free energy of the solution F is exactly similar to that obtained by the method of Debye and Hückel.

For a mixture of ionic species similar to that previously

¹ S. R. Milner, *Phil. Mag.*, **23** (vi) (1912), 551.

postulated, the mechanical work of dilution from V_1 to V_0 is :

$$\sum_i n_i kT \ln \frac{c_0}{c_1} - U_{el} = \sum_i n_i z_i e E = -F \quad . \quad (298)$$

where E is the potential difference due to the difference in concentration, and U_{el} is the Debye-Hückel expression for the effect of the ion atmosphere. Also

$$F = - \sum_i n_i kT \ln \frac{c_0}{c_1 f_1} \quad . \quad . \quad . \quad (299)$$

where f_1 is the activity coefficient of the solution at a concentration c_1 since the activity coefficient of the solvent is unity—*i.e.*, comparing values for F

$$\sum_i n_i kT \ln f = -U_{el} = - \sum_i \frac{n_i e^2 z_i^2 \kappa}{2D} \quad . \quad . \quad (300)$$

$$\text{or} \quad \ln f = - \sum_i \frac{e^2 z_i^2}{2(DkT)} \sqrt{4\pi e^2 n_i z_i^2} \quad . \quad (301)$$

since by (272)

$$\kappa = \sqrt{\frac{4\pi e^2}{DkT} \sum_i n_i z_i^2}$$

Introducing the ionic strength defined by equation (273)

$$\ln f = - \sum_i \frac{z_i^2 e^2 \sqrt{8\pi e^2 \mu}}{2(DkT)^{3/2}} \quad . \quad . \quad . \quad (302)$$

$$\text{or} \quad \ln f = -A \sum_i \frac{z_i^2 \mu^{1/2}}{(DT)^{3/2}} \quad . \quad . \quad . \quad . \quad (303)$$

where A is a numerical constant.

It follows from equation (303) for $\ln f$, that the activity coefficient of a strong electrolyte is dependent only on the ionic strength of the solution, and is therefore the same in all solutions of the same ionic strength. The interionic attraction theory therefore gives a definite proof of Lewis's important empirical rule (p. 181).¹ If only aqueous solutions are considered and the values for the appropriate constants are substituted, it is found for symmetrical electrolytes (*i.e.*,

¹ G. N. Lewis and M. Randall, *J. Amer. Chem. Soc.*, **43** (1921), 1112. "Thermodynamics" (McGraw Hill, 1923), p. 374.

for electrolytes in which the valencies of the two ions are equal) that

$$\left. \begin{aligned} \ln f &= 0.487 z^2 \mu^{\frac{1}{2}} \quad \text{at } 0^\circ \text{ C.} \\ \ln f &= 0.5056 z^2 \mu^{\frac{1}{2}} \quad \text{at } 25^\circ \text{ C.} \end{aligned} \right\} \quad (304)$$

Experimental Determinations of Activity Coefficients (Results).

The experiments which have been made both by direct determinations of the activity coefficients and by the activity effect on the solubilities of salts, with a view to verifying these

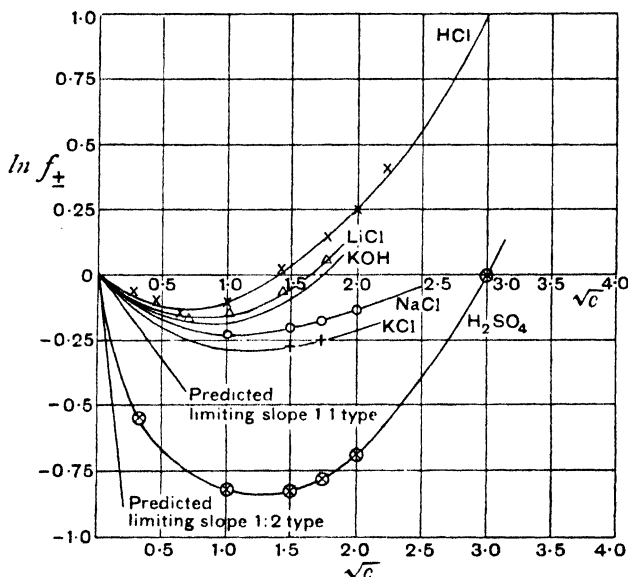


FIG. 58.—ACTIVITY COEFFICIENTS AS FUNCTION OF CONCENTRATION.

equations, give quite the most reliable test of the interionic attraction theory applied to the thermodynamic properties of ions. The activity coefficients of electrolytes may be most conveniently determined with the necessary accuracy from measurements of the E.M.F. of concentration cells of their solutions or from vapour pressure measurements made by the isopiestic method¹ (see Chapter VI). From measure-

¹ R. A. Robinson and D. A. Sinclair, *J. Amer. Chem. Soc.*, **56** (1934), 1830.

R. A. Robinson, *ibid.*, **59** (1937), 84.

ments which have been made in this way with uni-univalent salts, the expression predicted for the mean activity coefficient by the simple application of the ion atmosphere theory has been found to give approximately the limiting slope observed, but at higher concentrations the observed activity coefficient curves pass through a minimum and the coefficients become greater than unity at high concentrations (Fig. 58).¹ A positive term would therefore be needed at high concentrations in the expression for the activity coefficient, in order to make it account for the observed behaviour (see p. 210).

Solubility Effects.

The direct determinations of the activity coefficients suffer from the disadvantage that measurements cannot easily be made at the very low concentrations to which the simple theoretical expression for $\ln f$ in (302) can be applied with accuracy. Moreover, it is only possible to use the E.M.F. method in a limited number of cases where electrodes can be obtained which are completely reversible to both ions of the electrolyte. A much finer verification of the results of Debye and Hückel's simple theory of thermodynamic properties is available from a consideration of the effects of one electrolyte on the solubility of a saturated solution of another electrolyte having a common ion. According to classical dissociation theory, due to the common ion effect (*i.e.*, the repression of the dissociation of the electrolyte in solution), the addition of one electrolyte to a solution of another should always lower the solubility of this by causing some of the electrolyte to separate as a solid from the saturated solution. Due to interionic forces, however, there will be a greater tendency for ions to pass from the surface of the solid electrolyte into solution than for the reverse process to take place, and the net solubility effect due to the added electrolyte will therefore be determined by the relative magnitudes of the two effects, provided there are no complications due to complex ion formation.

Let us consider the simplest case of a di-ionic electrolyte.

¹ Lewis and Linhart, *J. Amer. Chem. Soc.*, **41** (1919), 1951.

We may first confine our attention to the equilibrium between the solid and the solution in the absence of any added electrolyte, introducing in our derivation the solubility product L . We will suppose that upon dissociation the electrolyte gives N_+ and N_- ions and that the concentrations of these are c_+ and c_- , their corresponding activity coefficients f_+ and f_- . From equation (177) the free energy of N_i molecules of a given species i may be represented by

$$\bar{F}_i = N_i \bar{F}_i^0 + N_i kT \ln (c_i f_i)$$

For a solution of the completely dissociated electrolyte, in which the subscript 0 is reserved for the solvent species, the total free energy of the solution is

$$\mathbf{F} = N_0 \bar{F}_0^0 + N_0 kT \ln (c_0 f_0) + \sum_1^2 N [\bar{F}^0 + kT \ln (cf)] \quad (305)$$

where N_0 is the number of molecules of solvent. For the transfer of one molecule of the solid from the solid to the solution, the change in free energy is therefore (N_0 being constant) :

$$\Delta \mathbf{F} = \sum_1^2 \Delta N [F^0 + kT \ln (cf)] \quad . \quad . \quad (306)$$

while the corresponding free energy change for the solid (activity constant) is :

$$\Delta \mathbf{F} = \sum_1^2 \Delta N \bar{F}^{0'} \quad . \quad . \quad . \quad (307)$$

At equilibrium the total free energy of the system has a stationary value—i.e. :

$$\Delta (\mathbf{F} + \mathbf{F}') = 0$$

or

$$\sum_1^2 [\bar{F}^0 + kT \ln (cf)] - \sum_1^2 \bar{F}^{0'} = 0 \quad . \quad . \quad (308)$$

or writing :

$$\ln K_t = \frac{1}{kT} \sum_1^2 (\bar{F}^{0'} - \bar{F}^0) \quad . \quad . \quad (309)$$

(308) becomes

$$\ln K_t = \sum_1^2 \ln (cf) \quad . \quad . \quad . \quad (310)$$

where K_i is a "solubility constant," depending on the temperature and pressure only, which determines the solubility of the pure electrolyte.

For the case under consideration of a simple di-ionic electrolyte, (310) becomes :

$$(c_+ f_+)(c_- f_-) = K_i \quad . \quad . \quad . \quad (311)$$

The solubility product for a simple di-ionic electrolyte is defined as :

$$L = c_+ c_- \quad . \quad . \quad . \quad (312)$$

From (311) and (312), therefore, the solubility constant and the solubility product are related as :

$$K_i = L f_+ f_- = L f_{\pm}^2 \quad . \quad . \quad . \quad (313)$$

where $f_{\pm}$ is the mean activity coefficient of the salt.

In the presence of a second electrolyte, where the equilibrium conditions for the pure electrolyte are disturbed, a similar expression will be obtained with the new concentrations $\bar{c}_+$, $\bar{c}_-$ and activities $\bar{c}_+ \bar{f}_+$, $\bar{c}_- \bar{f}_-$ of the ions of the solid phase. But since K_i , the solubility constant, has been so defined (309) as to be independent of this concentration

$$K_i = \bar{L} \bar{f}_{\pm}^2 \quad . \quad . \quad . \quad (314)$$

The ratio of the activity coefficients in the pure solvent and in the presence of the added electrolyte is therefore given from (313) and (314) by

$$\frac{\bar{L}}{L} = \left(\frac{f_{\pm}}{\bar{f}_{\pm}} \right)^2 \quad . \quad . \quad . \quad (315)$$

This relation, which has been deduced on the basis of a complete dissociation of the electrolyte, may readily be tested experimentally. The influence of the valency of the saturating salt is easily obtained from the expressions for the activity coefficient (304). Thus, denoting the ratio $\bar{L}/L$ in (315) by R_{11} for a 1 : 1 valent salt and by R_{13} for a 1 : 3 valent saturating salt, (315) becomes in the two cases, for the addition of the same concentration of solvent salt,

$$\left. \begin{aligned} \log R_{11} &= \log f_1^2 = (0.505)^2 \mu \\ \log R_{13} &= \log f_3^2 = (0.505)^2 (3)^2 \mu \end{aligned} \right\} \quad . \quad (316)$$

or
$$\frac{\log f_3}{\log f_1} = \frac{\log R_{13}}{\log R_{11}} = \left(\frac{3}{1} \right)^2 \quad . \quad . \quad . \quad (317)$$

Experimental Determinations of Solubility Effects.

An experimental verification of these results must be carried out with sparingly soluble salts in order that the concentrations shall be sufficiently low for (304) to apply. The salts used must therefore be capable of accurate analysis. The cobaltammines have proved to be the best saturating salts, since the large number of ammonia molecules in each molecule of this complex allow a ready analysis of the solutions to be made volumetrically. Thus from his measurements, Brönsted quotes the following example.¹ The solubility of a sparingly soluble uni-univalent salt in $M/20$ salt solutions of the same valency type, *e.g.*, KCl used as the "solvent salt"—shows on an average an increase of 20% above the solubility in pure water. Assuming that the activity coefficient f_1 in pure water is unity, then

$$\log f_1 = -\log 1.20 = -0.079$$

The trivalent salt luteo-cobaltic-hexa-cyano-cobaltate has its solubility raised in an $M/20$ solution of potassium chloride by 5.4 times above its value in pure water—*i.e.*,

$$\log f_3 = -\log 5.4 = -0.73$$

and from (317) therefore, we have :

$$\frac{\log f_3}{\log f_1} = \frac{0.73}{0.079} = \frac{9.2}{1} = \left(\frac{3.03}{1}\right)^2$$

showing that the ratio of the logarithms of the activities is almost equal to the ratio of the squares of the valencies.

The influence of the ionic strength on the activity coefficients has been observed by varying the type of the surrounding solvent salt. It is of course assumed here that the principle of equal activity coefficients in solutions of the same ionic strength applies accurately only in the limiting range. The relation becomes inconsistent at concentrations where the individual properties of the ions have a perceptible influence. Since from (273)

$$\mu = \frac{1}{2} \sum_i n_i z_i^2$$

¹ Brönsted and La Mer, *J. Amer. Chem. Soc.*, **46** (1924), 555.

and the equivalent concentrations are given by $\gamma_i = z_i n_i$, then :

$$\mu = \frac{1}{2} \sum_i z_i \gamma_i \quad . \quad . \quad . \quad . \quad . \quad (318)$$

where γ_i is the equivalent concentration of ions of the ionic species i , the ions of which all have a valency z_i . For a simple binary salt $\mu = \frac{1}{2} \gamma (z_1 + z_2)$ or, if n_1 be the number of cations and n_2 the number of anions in one molecule,

$$\frac{n_1}{z_2} = \frac{n_2}{z_1} = \frac{n_1 + n_2}{z_1 + z_2}$$

$$i.e., \quad \ln f = \frac{n_2}{n} \ln f_1 + \frac{n_1}{n} \ln f_2 = - A z_1 z_2 \mu^{\frac{1}{2}} \quad . \quad (319)$$

Only very complex substituted cobaltammines are found to satisfy all the required conditions as suitable saturating salts, and in Brönsted's determinations the solvents used were chosen from water and solutions of sodium chloride, potassium nitrate, potassium cobalticyanide, barium chloride, magnesium sulphate, and potassium sulphate, although not necessarily all of these could be used for any one saturating salt. Each solvent salt gives a different point on the $\log f$ against square root of the ionic strength curve, and the valency effect of the saturating salt is very well illustrated by plotting the curves for the three valency types :

uni-univalent salt $[\text{Co}(\text{NH}_3)(\text{NO}_2)(\text{CNS})][\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]$

di-univalent salt $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]_2[\text{S}_2\text{O}_6]$

tri-univalent salt $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]_3$

The solubilities of these in the saturated solutions were determined by Brönsted and La Mer by adding sufficient alkali to expel all the ammonia into a known quantity of very dilute hydrochloric acid, the excess acid being back-titrated against alkali. Owing to the large number of ammonia molecules which are thus liberated from one molecule of a cobaltammine, the solubility of these compounds could be determined with considerable accuracy.

The types of curves obtained are illustrated in Fig. 59 for the 1·1, 1·2, and 1·3 valent salts. It will be seen that Brönsted's experiments show that the linear relation between $\log f$ and $\sqrt{\mu}$ is obeyed up to concentrations of about 0·01M

and down to the lowest concentrations at which determinations of the solubility have been made; also that the constant term in the theoretical expression predicts the effects quantitatively at the lowest concentrations. A number of further determinations using the same method have been carried out by La Mer ¹ which show that only the particular type of salts chosen by Brönsted and La Mer gave results conforming

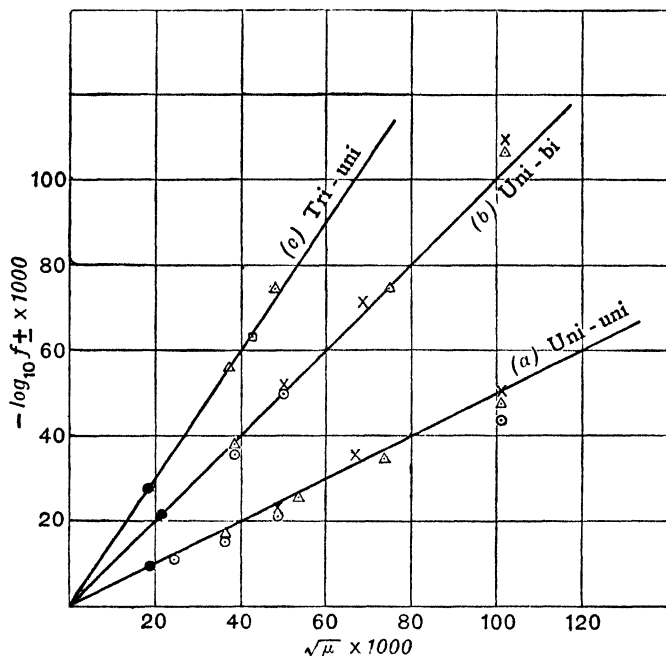


FIG. 59.—ACTIVITY COEFFICIENTS OF COMPLEX COBALT SALTS FROM SOLUBILITY MEASUREMENTS.

very well with the Debye theory. A number of other salts, all of them, however, of unsymmetrical valency types, such as $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]_3$, when investigated in solutions of electrolytes containing other than uni-univalent anions, did not show a linear law between $\log f$ and $\sqrt{\mu}$. In these cases the experimental lines cross the theoretical curves

¹ La Mer, C. V. King, and C. F. Mason, *J. Amer. Chem. Soc.*, **49** (1927), 363, 410.

La Mer and F. H. Goldman, *ibid.*, **51** (1929), 2632.

twice, and the limiting slopes are much steeper than those calculated by the Debye theory (Fig. 60).

These variations for unsymmetrically valent salts, however, appear in other thermodynamic properties of strong electrolytes, and the effect may be due to the importance of solvation and association of the ions in the solutions of salts of complex valency types. The predicted effect of the dielectric constant of the solution on the activity coefficients has been confirmed in a general way from measurements by the

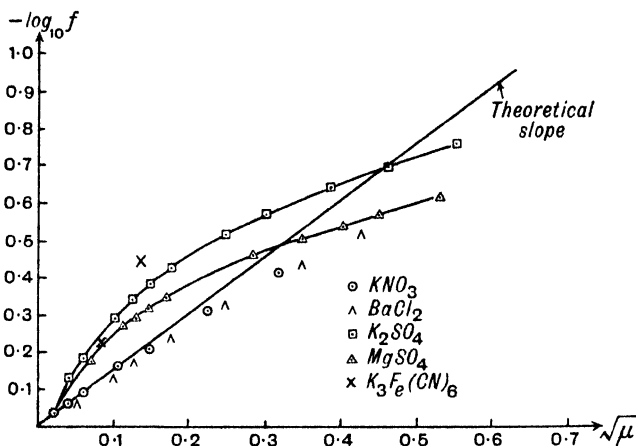


FIG. 60.—THE ACTIVITY COEFFICIENTS OF THE UNSYMMETRICAL SALT $[Co(NH_3)_6][Co(NO_2)_2(NH_3)_3C_2O_4]_3$ IN SALT SOLUTIONS.

E.M.F. method in the alcohols and mixtures of the alcohols with water. The results show that over the whole range of dielectric constants so obtainable $\log f$ is approximately proportional to $1/(DT)^{\frac{1}{2}}$.¹ In solvents of lower dielectric constant than water the theoretical equation applies over an even more limited range than in aqueous solutions, the effect of the decrease of dielectric constant being qualitatively the same as an increase in the valency type of the salt.

An empirical theory accounting for the specific variations in solubility effects among electrolytes, was put forward by

¹ Nonhebel and H. Hartley, *Phil. Mag.*, **30** (vi) (1925), 729.

Butler and Robertson, *Proc. Roy. Soc., A*, **125** (1929), 694.

Brönsted in 1922¹ before the work of Debye and Hückel, and, unlike the latter, it could be applied to mixtures. Brönsted supposed that in a solution containing both positive and negative ions, since ions of similar size repel one another, these will never come sufficiently closely together for their specific structures to affect their behaviour in the solution. For ions of opposite sign, however, there will be "specific interaction" which will depend on the specific ions present, and not only upon the valency types of the ions present. Brönsted developed the theory using a method by which the individual ion activities were introduced. Exception has been taken to this on the ground that individual ion thermodynamic functions have no physical meaning (see p. 168), but the same results have been obtained using an unequivocal statistical method.² If some arbitrary standard salt is chosen, it will be possible in any actual case to divide up the mutual interionic energy $W_{\alpha\beta}$ between two ions α and β into the energy $W_{\alpha\beta}^0$ due to Coulomb forces and the energy $W_{\alpha\beta}'$ due to short range forces. Thus

$$W_{\alpha\beta} = W_{\alpha\beta}^0 + W_{\alpha\beta}'$$

and so also, for the contribution of the interionic energy F_{el} to the free energy F_{el} ,

$$F_{\text{el}} = F_{\text{el}}^0 + F_{\text{el}}^1$$

For short-range forces it has been shown that, in general.

$$F_{\text{el}}' = \frac{1}{V} \sum_{\alpha, \beta} n_{\alpha} n_{\beta} \epsilon_{\alpha\beta}$$

where $\epsilon_{\alpha\beta}$ is a constant for a given medium, temperature and ion pair $\alpha\beta$. Now, using Brönsted's principle, that short-range forces are important only for ions of opposite charge (cations c and anions a) we have :

$$F_{\text{el}}' = \frac{1}{V} \sum_{c, a} n_c n_a e_{ca}$$

¹ J. N. Brönsted, *J. Amer. Chem. Soc.*, **44** (1922), 877; **45** (1923), 2898.

² E. A. Guggenheim, Report 18th Scandinavian Congress (1929), Copenhagen.

Also, for a salt AB , the activity coefficient f_{AB} is defined by :

$$2RT \ln f_{AB} = \left(\frac{\partial F_{el}}{\partial n_A} \right) + \left(\frac{\partial F_{el}}{\partial n_B} \right)$$

or from (177)

$$\ln f_{AB} = \frac{1}{2RT} \left(\frac{\partial F_{el}^0}{\partial n_A} \right) + \frac{1}{2RT} \left(\frac{\partial F_{el}^0}{\partial n_B} \right) + \sum_{\text{anions}} \frac{n_a}{V} \cdot \frac{\epsilon_{Aa}}{2RT} + \sum_{\text{cations}} \frac{n_c}{V} \cdot \frac{\epsilon_{Bc}}{2RT}$$

$$\text{or} \quad \ln f_{AB} = \ln f^0 + \sum_{\text{anions}} \frac{n_a}{V} \cdot \frac{\epsilon_{Aa}}{2RT} + \sum_{\text{cations}} \frac{n_c}{V} \cdot \frac{\epsilon_{Bc}}{2RT}$$

Denoting by x_{ac} the number of moles of anions, where c is the total concentration of salt, the equation for $\ln f_{AB}$ becomes :

$$\ln f_{AB} = \ln f^0 + \sum_{\text{anions}} k_{Aa} x_{ac} + \sum_{\text{cations}} k_{Bc} x_{Bc}$$

where

$$k_{a\beta} = \frac{\epsilon_{a\beta}}{2RT}$$

This equation for $\ln f_{AB}$ expresses the principle of linear variation of activity peculiarities which Brönsted adduced from his theory of specific interaction.¹ From it, many relations have been obtained for the ratios of activity coefficients of salts in mixtures and for the activity coefficients of one salt in the presence of another. These relations have been confirmed very well for 1:1 valent salts from the solubility measurements of Brönsted and the equations may be applied with certain reservations to more complexly valent salts.²

Activity Coefficients in More Concentrated Solutions.

Due to the fact that there is a very intense field in the immediate vicinity of an ion, it is very unlikely that the

¹ Brönsted, *J. Amer. Chem. Soc.*, **45** (1923), 2898.

² References on pp. 204 *et seq.* The theory has been applied by Guggenheim to the osmotic coefficients of electrolytes and mixtures of electrolytes, by attempting to unite the useful features of Brönsted's principle and of Debye and Hückel's analysis. The equations allow for specific differences between electrolytes of the same valency type and are in good agreement with the best data for the osmotic coefficients of single electrolytes (Guggenheim, *Phil. Mag.*, **19** (vii) (1935), 588; see also E. Güntelberg, *Z. physikal. Chem.*, **123** (1926), 199).

dielectric constant remains the same in this vicinity as in the body of the solution. Equation (267) will therefore have to be modified to take this into account, and the value for $\ln f$ will therefore not be given by equation (302). Now, the dielectric constant is a measure of the polarisation produced in a medium by an applied field. It may therefore be divided into two parts, one part due to the electric charges which become separated in the molecule under the electric field, the other due to the orientation polarisation of the permanent dipoles in the medium.¹ The polarisation due to orientation will rapidly approach a constant value as the field is increased, due to the unilateral orientation of all the dipoles. Again, the induced polarisation due to the separation of charges within the molecule is so great in intense fields that it is no longer proportional to the field strength. In the immediate vicinity of an ion, therefore, the dielectric constant will no longer have the value associated with the pure solvent. From a consideration of the possible variations in the dielectric constant of the solution with the salt concentration, Hückel obtained an expression for the activity coefficient²

$$\ln f = -\frac{\alpha\sqrt{\mu}}{1 + \beta\sqrt{\mu}} + D\mu \quad . \quad . \quad (320)$$

which, since it contains a positive term $D\mu$, will be able, for suitable values of the constants, to give positive values of the activity coefficient at high concentrations, agreeing qualitatively with the experimental observations. The observed variations of $\log f$ with the concentration³ show, however, that equation (320) does not predict these variations quantitatively if the calculated values of the constants are used. But, although this renders the equation more arbitrary than was at first supposed, a suitable choice of constants in the above equation can be made such that it predicts the observed variations of $\ln f$ quite accurately up to relatively high concentrations ($1N$).

¹ Debye, "Polar Molecules," 1929, pp. 15 and 29.

² Hückel, *Physikal. Z.*, **26** (1925), 93.

Butler, *J. Physical Chem.*, **33** (1929), 1015, accounts for the linear term in Hückel's equation (217) for $\ln f$ by supposing the ions to have a "salting-out" effect upon one another.

³ *E.g.*, G. Scatchard, *J. Amer. Chem. Soc.*, **47** (1925), 641, 2098.

For the activity coefficients in solutions of non-electrolytes, the empirical expression

$$\ln f = -\beta\mu \quad . \quad . \quad . \quad . \quad (321)$$

predicts a linear salt effect between a charged and an uncharged molecule which is very well borne out by experiment.¹ This linear salt effect may be explained qualitatively in terms of the relative polarisabilities of the solvent molecules—i.e., of the solvent proper and of the solvent non-electrolyte. For aqueous solutions, water will almost always be the more polarisable component, and it will therefore form agglomerates round the ions of the salt added, increasing the proportion of the less polarisable solute molecules at a distance from the ions, and therefore affecting their activity.²

The Heat of Dilution.

A further application of the Debye theory to the thermodynamic properties of solutions of strong electrolytes has resulted in the prediction of the heats of dilution. The experimental work which has been rendered necessary in order to confirm the theoretical equations has included some of the most careful and accurate work of recent years in the field of experimental physical chemistry. If the integral heat of dilution be denoted by V_c , then V_c is the heat obtained on diluting the solution from a concentration c to infinite dilution, a quantity which can never be measured experimentally. If, however, V_c is calculated, the determination of the heat of dilution from c_1 to c_2 may be carried out and the value of $V_{c_1} - V_{c_2}$ calculated. The heat of such a process corresponds to the reversible free energy of dilution, and the heat of dilution is to the free energy of dilution as the heat of a chemical reaction is to the free energy obtained in carrying out the reaction in a cell. Applying therefore the Gibbs-Helmholtz equation (156) :

¹ V. Rothmund, *Z. physikal. Chem.*, **33** (1900), 401; **69** (1909), 523.

² McAulay, *J. Physical Chem.*, **30** (1926), 1202.

$$H = \text{Irreversible heat of dilution} = F - T \left(\frac{\partial F}{\partial T} \right)_P \quad (322)$$

$$H = F_{\text{id.}} + F_{\text{el.}} - T \left(\frac{\partial F_{\text{id.}}}{\partial T} \right)_P - T \left(\frac{\partial F_{\text{el.}}}{\partial T} \right)_P \quad (323)$$

For the ideal solution therefore

$$F_{\text{id.}} - T \left(\frac{\partial F_{\text{id.}}}{\partial T} \right)_P = 0 \quad . \quad . \quad . \quad (324)$$

Now, on dilution of an electrolyte solution, only the electrical contribution to the heat of dilution is measured—i.e. :

$$V_c = F_{\text{el.}} - T \left(\frac{\partial F_{\text{el.}}}{\partial T} \right)_P \quad . \quad . \quad . \quad (325)$$

$$V_c = - \sum_i \frac{kT\kappa^2 V}{24\pi} - T \left[- \sum_i \frac{k\kappa^3 V}{24\pi} - \sum_i \frac{3k\kappa^3 V}{24\pi} \frac{\partial \kappa}{\partial T} \right] \quad (326)$$

$$V_c = \sum_i \frac{kT\kappa^2 V}{8\pi} \cdot \frac{\partial \kappa}{\partial T} \quad . \quad . \quad . \quad (327)$$

where by (272) $\kappa^2 = \frac{4\pi^2 e}{DkT} \cdot \sum_i n_i z_i^2$

Putting $\kappa = \lambda/(DT)^{\frac{1}{2}}$ where λ is independent of the temperature and differentiating (272), we have :

$$\begin{aligned} \frac{\partial \kappa}{\partial T} &= - \frac{\lambda}{2} \left[\frac{1}{(DT)^{\frac{1}{2}} T} + \frac{1}{D(DT)^{\frac{1}{2}}} \frac{\partial D}{\partial T} \right] \\ &= - \frac{\kappa}{2T} \left(1 + \frac{T}{D} \frac{\partial D}{\partial T} \right) \quad . \quad (328) \end{aligned}$$

i.e., substituting in (327) :

$$V_c = - \sum_i \frac{N_0^{\frac{1}{2}} z_i^2 e^3}{2D^{\frac{1}{2}} (kT)^{\frac{1}{2}}} \sqrt{8\pi} \sqrt{\gamma} \left[1 + \frac{\partial D}{\partial T} \cdot \frac{T}{D} \right] \quad . \quad (329)$$

since

$$\gamma N_0 = V n_i$$

If γ , the equivalent concentration, be expressed in gram-molecules per litre, a factor $\sqrt{1000}$ will have to be introduced into the denominator giving :¹

$$V_c = - \sum_i \frac{N_0 e^2 z_i^2}{2D} \sqrt{\frac{8\pi N_0 e^2 z_i^2}{1000 D k T}} \left[1 + \frac{\partial D}{\partial T} \cdot \frac{T}{D} \right] \gamma^{\frac{1}{2}} \quad . \quad (330)$$

¹ O. Gatty, *Phil. Mag.*, 11 (1931), 1082, and G. Scatchard, *J. Amer. Chem. Soc.*, 53 (1931), 2037, have shown that strictly this expression should include a third term $\frac{T}{3V} \left(\frac{\partial V}{\partial T} \right)_P$ which allows for the difference between $\left(\frac{\partial D}{\partial T} \right)_P$ and $\left(\frac{\partial D}{\partial T} \right)_V$.

calories per mole. On investigation, $\partial D/\partial T$ is found to be negative for all substances ¹ and of such a value that

$$\frac{T}{D} \frac{\partial D}{\partial T} < -1$$

Considerable uncertainty, however, attaches to the values of $\frac{\partial D}{\partial T}$,² and values for $1 + \frac{\partial \log D}{\partial \log T}$ are extremely sensitive to small differences in this temperature coefficient of the dielectric constant. In aqueous solutions

$$1 + \frac{\partial \log D}{\partial \log T} = \left[1 + \frac{\partial D}{\partial T} \cdot \frac{T}{D} \right]$$

has been given values ranging from -0.256 to -0.471 , so that it cannot be hoped to predict theoretically numerically exact results, for an adequate quantitative verification of the theory for heats of dilution would require a knowledge of the value of $\partial D/\partial T$ to an accuracy of at least $\pm 0.05\%$.

The equation for V_e , however, predicts that heats of dilution should always be positive and proportional to the square root of the concentration in the limiting range, and that for all electrolytes of the same valency types the heats of dilution should be the same in the limiting range. These predictions are quite contrary to expectation. For, as a consequence of the ion atmosphere, negative heats of dilution might have been expected quantitatively, due to the apparent work necessary to separate the ions. The factor $\frac{\partial D}{\partial T}$ depends roughly on the dipole moment of the solvent molecules, and it is due to the influence of the ions on the dipoles of these (which more than compensates the energy absorbed during dilution, by the increasing separation of the ions) that the heat effect remains positive over a small range of low concentrations to which the simplified electrostatic picture may be applied with some accuracy.³

¹ Wyman, *Physical Rev.*, **35** (1930), 623.

Lathey, Gatty and Davies, *Phil. Mag.*, **2** (vii) (1931), 1019.

² Lange and Robinson, *J. Amer. Chem. Soc.*, **52** (1930), 2811.

³ Bjerrum, *Z. physikal. Chem.*, **119** (1926), 145.

Experimental Determinations of Heats of Dilution.

Of the experimental work on the heats of dilution previous to 1927, when Lange began his measurements,¹ that of Richards and Rowe on uni-univalent salts only was the most accurate.² Their measurements were carried out over a range of concentrations down to 0.139M, and the results are best expressed by plotting $V_c - V_{0.139}$ against the square root of the concentration. Some of the measurements of Richards expressed in this way are shown in Fig. 61. The curves illustrate well the way in which the majority of uni-

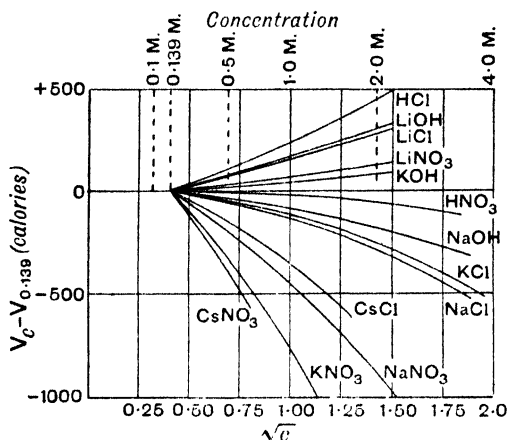


FIG. 61.—HEATS OF DILUTION OF VARIOUS SALTS (Richards).

univalent electrolytes studied showed negative heats of dilution over the whole range of concentration.³ Thus, while hydrochloric acid diluted from normal to 0.139N gives out about 500 calories, the dilution of sodium chloride, potassium nitrate, and sodium hydroxide over a similar range give negative heats of dilution. It is notable that for all these electrolytes over a range from about 0.02 to 0.139N, the osmotic coefficients show quite fair agreement with the Debye theory. This anomaly in the case of the heats of dilution may be due to the importance of ion-solvent forces

¹ E. Lange and G. Messner, *Naturwiss.*, **15** (1922), 54.

² T. W. Richards and Rowe, *J. Amer. Chem. Soc.*, **43** (1921), 770; *Z. physikal. Chem. (A)*, **119** (1926), 158.

³ N. Bjerrum, *Trans. Faraday Soc.*, **23** (1927), 445.

(depending as they do on the variation of the dielectric constant with temperature) in the heats of dilution. The extent to which they affect the other thermodynamic properties of the electrolyte solution, on the other hand, is greatly reduced by the predominating influence of the ion-ion forces.

Evidently, therefore, it was necessary to be able to determine the heats of dilution over a range of much smaller concentrations where the Debye theory holds, than with the other osmotic properties of electrolyte solutions,—viz., from about $N/100$ to $N/1000$. In this range an approximate calculation of the magnitude of the effect may be made, for if

$$\sqrt{c_1} - \sqrt{c_2} \approx 0.1 - 0.03 = 0.07$$

then

$$V_{c_1 - c_2} = 490[\sqrt{c_1} - \sqrt{c_2}] \quad . \quad . \quad . \quad (331)$$

for uni-univalent electrolytes. The value 490 for the constant in equation (330) is taken as an approximate mean of the extreme values—i.e., the approximate heat of dilution is $V_{c_1 - c_2} = 34.3$ calories. If this has to warm 1000 litres of $N/1000$ solution containing 1 gram-mole of the substance, the increase in temperature will be only about 0.34×10^{-4} degrees. Now, even the slowest stirring necessary to maintain a uniform temperature would in about twelve seconds cause a heat change greater than the heat quantity to be measured, and the evaporation of one-tenth of a milligram of water causes a heat change in this volume greater than the heat of dilution. There is therefore only one method which may be used to avoid the effect of these unbalanced effects, viz. the use of a differential calorimeter having the solution on one side and pure solvent on the other, separated in the same calorimeter by a suitable frame carrying a large number of differential thermocouples. The method was first used by Nernst and Orthmann,¹ who had in their apparatus all the essentials for an accurate determination, but who did not bring their experimental technique to the same degree of refinement as did Lange and his collaborators.² The calorimeter employed

¹ Nernst and Orthmann, *Ber. Berlin Akad.* (1926), 51; (1927), 136.

² A review of a large number of papers published by Lange and his collaborators is given by Lange and Robinson, *Chem. Rev.*, **9** (1931), 89.

by these latter workers consisted of a Dewar vessel (Fig. 62) around the inside of which was a frame *B* arranged to

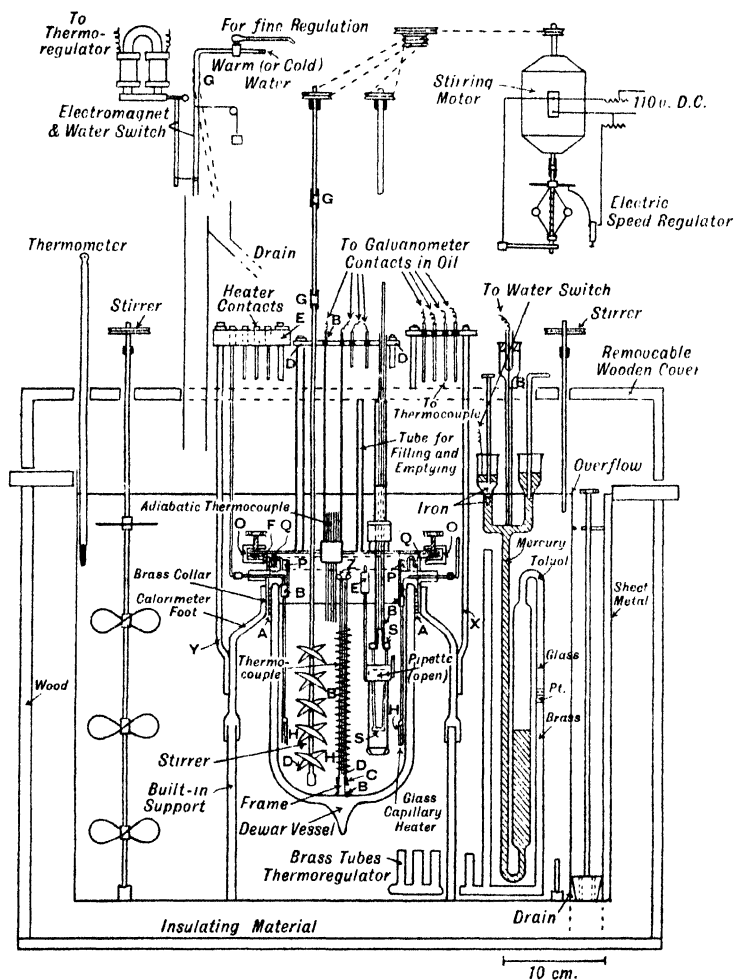


FIG. 62.—LANGE'S ADIABATIC DIFFERENTIAL CALORIMETER.

divide the vessel into halves. To this was cemented a hard sheet *D* through which passed the wires of the thermojunctions numbering perhaps 1000, each protected by a small glass cap. In each compartment an exactly similar stirrer

was driven from the same regulated motor at the same speed in opposite directions, so that the heating effects due to these counterbalanced. Each side of the calorimeter had also a glass capillary heater *H*, the lead of which passed out through the side disc *P*. The solvent side had a series of thermocouples, one end in the solvent, the other in the liquid of the constant-temperature bath in which the calorimeter was immersed. This thermocouple registered a current when the temperature of the bath and that of the solvent were not identical, and this could be amplified and passed to a small electromagnetically operated water-switch. When the current passed, this was deflected so that cold water flowed into the bath until equality of temperature with that of the solvent was again restored. A similar set of thermocouples, which was not, however, connected up, was fitted to the right-hand side of the vessel to compensate any effect on the temperature of the solvent which might be caused by the presence of the thermocouples on the solvent side. The dilution itself was carried out both on the solvent and on the solution by means of the special pipette which contained the solvent on the solvent side of the calorimeter and strong solution on the other side. These pipettes were of thin metal, and the plugs *SS*, which fitted accurately into the ends of the pipette cylinder, could be pulled up simultaneously on both sides by connecting the rods *K* together. On the solution side the dilution was therefore carried out by adding solution to pure solvent. In order to avoid or reduce heat effects due to absorption on the inner wall of the Dewar vessel, this was in some cases covered with a thin layer of vaseline. The similar coils *H* of constantan wire were used to supply known quantities of electrical energy on one side when the heats of dilution for concentrated solutions became inconveniently large on the galvanometer scale. The amount of energy supplied could then be regulated until the deflections were again of convenient dimensions. With pure water on both sides and in both pipettes, it was found that, on releasing only one of these—as, for example, on diluting water with water—the galvanometer gave a small kick which could be traced to the fact that, by stirring, the temperature of the

water on each side had become slightly higher than in the pipette. Simultaneous dilution of solvent with solvent on both sides gave equal temperature effects, so that the galvanometer remained steady.

In order to determine the water equivalent of the calorimeter, a known current was passed through the coils H for about four seconds first on one side, then on the other. The individual heat capacities could then be calculated from a knowledge of the quantities of solvent present and its rise of temperature. During the course of the experiments it was necessary that the temperature coefficient across the dividing plate should be small in order to prevent thermal leakage across this, but this condition could always be assured by a suitable choice of substance from which to construct the plate.

The types of curve obtained for the experimentally determined values of V_c , the integral heat of dilution, when these are plotted against the square root of the concentration, are illustrated in Fig. 63 for the uni-uni- and di-univalent salts. The broken lines show the theoretically obtained curves from Debye's theory and from the theory of Gronwall, Sandved and La Mer using different values of the parameter " a " (see pp. 220, 222). The range over which the square-root law is applicable with any degree of accuracy is far less for uni-univalent than for di-univalent salts, terminating even for the best uni-univalent salts at about 0.01N. The limiting slopes for all the di-univalent salts are approximately those predicted, and all salts of this type have approximately the same limiting slopes. There is, however, as already stated, considerable uncertainty in the predicted values, due to small errors in the measurement of $\partial D/\partial T$, which have a large effect on the term $1 + \frac{\partial \log D}{\partial \log T}$. But, although uncertainties in the predicted value of the limiting slopes may account for the lack of agreement between these observed slopes, the Debye equation does predict that for all salts of the same valency type all the limiting slopes should be the same—and curves which cut near the limiting range (Fig. 59) cannot fulfil this condition. Again, the appearance of negative heats of dilution for KNO_3 and CsCl and KCl , even at quite

low concentrations, is quite out of agreement with the theory. For this one thermodynamic property, therefore, altogether much better agreement between the experimental and theoretical results is observed for unsymmetrically valent salts, particularly those of the di-univalent type. The general conclusion of Lange's work appears, therefore, to be that the limiting heats of dilution, although positive and

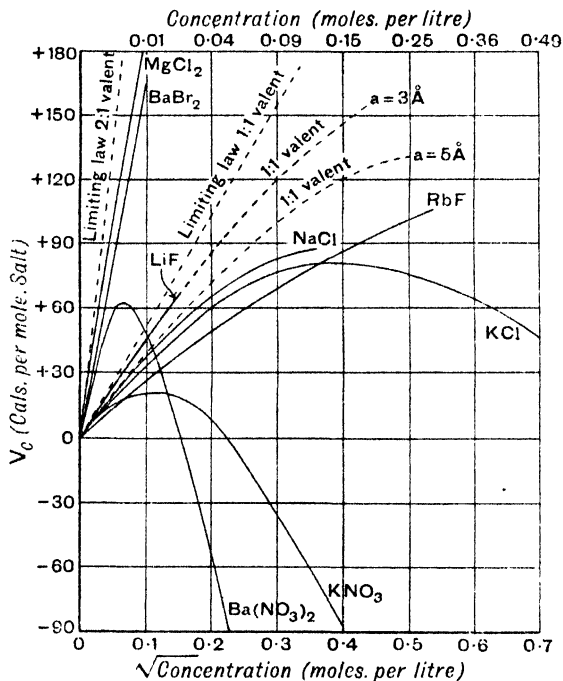


FIG. 63.—HEATS OF DILUTION AS A FUNCTION OF CONCENTRATION.

obeying the predicted valency and concentration effects in a general way, yet show residual individualities which cannot be explained by Debye's electrostatic theory even in the region of the highest dilutions. It should be noted that over the ranges of low concentrations where the heats of dilution fail to conform to the Debye law, the activity and osmotic coefficients, for example, can be predicted with greater accuracy. It has already been suggested (p. 215) that the individuality in thermochemical properties may be due to the

predominant part played here by the ion solvent as opposed to the usual ion-ion forces.

The Debye-Hückel Theory. Second Approximation.

The observed curves for the heats of dilution at higher concentrations show that negative values of V_c are quickly reached for many electrolytes. This behaviour is the opposite from that predicted by the Debye theory, and it is in common with the observed behaviour of all strong electrolyte solutions in all but the lowest concentrations. It is evident, therefore, that, outside the "limiting range," the simple analysis of the interionic attraction theory, as it was worked out by Debye and Hückel, cannot be applied without some modification or extension either of the mathematical analysis or of the physical ideas underlying the simple theory. Debye and Hückel made a "second approximation" in order to extend the range of concentration to which their theory would apply. They attempted to allow for the finite sizes of the ions which should have an appreciable effect on the value of the free energy, when they are appreciable compared with the effective size of the ion atmospheres.¹ In general, the ions are surrounded by small clusters of solvent molecules within which the dielectric constant is D . Their radius, which does not necessarily bear any relation to the ionic radius, will represent the closest mean distance of approach of the positive and negative ions. In their second approximation Debye and Hückel assumed that only in very strong solutions was the dielectric constant of the solution appreciably different from that of the pure solvent,² and the total potential just inside the ion cluster at a distance r from the centre was therefore

$$\psi = \frac{ze}{Dr} + B$$

and that just outside, $Ae^{-\kappa r}/r$. Since the dielectric constant was assumed to be the same inside as it was outside, the boundary conditions at the surface of separation of two

¹ Debye and Hückel, *Physikal. Z.*, **24** (1923), 184.

² Debye and Pauling, *J. Amer. Chem. Soc.*, **47** (1925), 2120.

dielectrics give that $\bar{\psi}$ and $\partial\bar{\psi}/\partial r$ shall be continuous—*i.e.*, at the boundary ($r = a$)

$$\frac{Ae^{-\kappa a}}{a} = \frac{e}{Da} + B$$

$$Ae^{-\kappa a} \frac{1 + \kappa a}{a^2} = \frac{e}{Da^2} \quad . \quad . \quad . \quad . \quad . \quad (332)$$

$$\text{i.e.,} \quad A = \frac{e}{D} \frac{e^{-\kappa r}}{(1 + \kappa a)} \text{ and } B = - \frac{e\kappa}{D(1 + \kappa a)} \quad . \quad (333)$$

B is equal to the potential due to the ion atmosphere, for on removing the central ion to infinity $\bar{\psi} = B$. The potential energy at the central ion due to the surroundings is therefore

$$\bar{\psi}_{II} = - \frac{ze\kappa}{D(1 + \kappa a)} \quad . \quad . \quad . \quad (334)$$

which reduces to the ordinary value given by (269) in dilute solutions, where κ is small and $1 + \kappa a \approx 1$. For high concentrations, however, this expression for the potential energy becomes $-ze/Da$, where “ a ” instead of the κ of the simple theory, is the “effective thickness” of the ion atmosphere.

The result of taking into account the actual size of the ions is therefore to introduce a factor $1/(1 + \kappa a)$ into any expression derived by assuming point charges. Values of the osmotic coefficient may be deduced with this new approximation, and the theoretical values obtained for the former are in particularly good agreement with the experimental values, as, *e.g.*, for MgSO_4 , K_2SO_4 and KCl , the values of “ a ” being determined from a few measurements in the extended region of applicability. In Fig. 59 the good agreement for a suitable choice of “ a ”, between the extended theory and experimental measurements is shown for $\text{La}_2(\text{SO}_4)_3$. Unfortunately the values of the diameter “ a ”, which are needed to make this extended theory fit the observed experimental values for the properties of strong electrolytes in more concentrated solutions, are frequently physically quite impossible, being in some cases negative (*e.g.*, those required for the activity coefficients of the alkali nitrates).¹

¹ Scharrer, *Physikal. Z.*, 25 (1924), 145.

V. K. La Mer, C. V. King and C. F. Mason, *J. Amer. Chem. Soc.*, 49 (1927), 363, 410.

Extended Theory of Gronwall, Sandved and La Mer.

Gronwall, Sandved, and La Mer¹ have carried out a more extended investigation of the higher approximations in Debye and Hückel's theory. These authors evaluated the potential $\bar{\psi}$ in terms of a convergent infinite series obtained by using the unabbreviated values of $\sinh ez_i\bar{\psi}/kT$ in (255) after substitution in the Poisson-Boltzmann equation. Their fundamental equation was therefore

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \bar{\psi}}{\partial r} \right) = \frac{8\pi z_i e N}{D} \sinh \frac{ez_i \bar{\psi}}{kT} \quad . \quad . \quad (335)$$

This equation may conveniently be transformed into a simpler form by substituting,

$$\left. \begin{aligned} \kappa &= \sqrt{\frac{8\pi e^2 z_i^2 N}{DkT}} \\ \rho &= \kappa r \\ x &= \kappa a \\ y &= \frac{z_i e \bar{\psi}}{kT} \\ b &= \frac{z_i^2 e^2}{DkTa} \end{aligned} \right\} \quad . \quad . \quad . \quad (336)$$

and

The Poisson-Boltzmann equation (335) then becomes :

$$\frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left(\rho^2 \frac{\partial y}{\partial \rho} \right) = \sinh y \quad . \quad . \quad . \quad (337)$$

with appropriate boundary conditions.² The method used by Debye and Hückel in their limiting theory was to make the approximation $\sinh y \simeq y$. Gronwall, and Gronwall La Mer and Sandved give the complete solution of the equation (337) in terms of a power series in κa .

Equation (337) may be rewritten :

$$\frac{\partial}{\partial \rho} \left(\rho^2 \frac{\partial y}{\partial \rho} \right) - \rho^2 y = \rho^2 \phi(y) \quad . \quad . \quad . \quad (338)$$

where $\phi(y) = \sinh y - y = \sum_{n=1}^{\infty} \frac{y^{2n+1}}{(2n+1)!} \quad . \quad (339)$

¹ Gronwall, *Proc. Nat. Acad. Sci. Washington*, **13** (1927), 198.

Gronwall, Sandved and La Mer, *Physikal. Z.*, **39** (1928), 358.

La Mer, Gronwall and Grief, *J. Physical Chem.*, **35** (1931), 2245.

² We use the nomenclature of Fowler, "Statistical Mechanics," 1936, pp. 550, 557.

By forming Green's function for the differential operator on the left-hand side of equation (338), an integral equation,

$$y(\rho) = \frac{bx}{1+x} \frac{e^{x-\rho}}{\rho} - \frac{1}{2\rho} \int_x^\infty \left\{ e^{-|t-\rho|} + \frac{x-1}{x+1} e^{2x-t-\rho} \right\} \phi[y(t)] t dt \quad (340)$$

is obtained. This may be verified by differentiation, having regard to the boundary conditions—viz., at $\rho = x$,

$$\frac{\partial y}{\partial \rho} = \frac{b}{x}$$

and y tends to zero as ρ tends to infinity.

The Debye-Hückel approximation considers only the first of the terms on the right-hand side of equation (340). To evaluate the integral, the crude solution in ϕ is first substituted, and as κ (and therefore x) approaches zero, this function is of the order x^2 . Gronwall expands the function y and shows that the terms now neglected are of the order $x^2 \ln x$. Approximately therefore

$$\begin{aligned} y(x) &\simeq \frac{b}{1+x} - \frac{1}{1+x} \int_x^\infty e^{x-t} \phi \left\{ \frac{b}{1+x} \frac{e^{x-t}}{t} \right\} b dt \\ y(x) &\sim b(1-x+x^2) - \sum_{n=1}^\infty \frac{(bx)^{2n+1}}{(2n+1)!} \int_x^\infty e^{2(n+1)(x-t)} t^{-2n} dt \\ y(x) &\simeq b(1-x-x^2) - x^2 \sum_{n=1}^\infty \frac{b^{2n+1}}{(2n+1)!(2n-1)} \end{aligned} \quad (341)$$

Remembering that $x = \kappa a$ and $b = \frac{z^2 e^2}{DkTa}$, we have therefore

$$\begin{aligned} \psi(a) &\simeq \frac{z_i e}{Da} \\ &- \frac{z_i e \kappa}{D} \left(1 - \kappa a + \kappa a \sum_{n=1}^\infty \frac{\left(\frac{z_i^2 e^2}{DkTa} \right)^{2n}}{(2n+1)!(2n-1)} \right) \end{aligned} \quad (342)$$

In equation (342) the potential due to the distribution round the central ion is given by the second term on the right-hand side. From the potential, the work function Ψ and hence the free energy of the solution $\partial \Psi / \partial v$ may be calculated.

The calculations for the activity coefficients, which are

very laborious, have been made for a number of salts and the values for " a " which are required in this extended theory are always reasonable, for even if the " a " values required by Debye and Hückel's theory are large and negative, the new " a " values still remain positive when describing the same conditions. The theory also predicts a difference in the behaviour of symmetrically and unsymmetrically valent electrolytes, as observed by experiment. Nevertheless the values of " a " which have to be used, to make Gronwall's predicted functions fit the experimental results, seem to show no analogy with the values for the ionic radius in solution, when these are calculated from the mobilities, etc. Moreover, the " a " values in Gronwall's theory are not mutually consistent when the equations are applied to the different thermodynamic functions of an electrolyte. For example, the values required to bring the calculated osmotic coefficients into line with the results obtained from freezing-point measurements for magnesium, barium, calcium and strontium salts, are in the reverse order from those required to correlate the experimental and predicted values for the heats of dilution of the same salts.

There are other objections to this and similar attempts, to extend Debye and Hückel's theory without introducing new physical assumptions. Gronwall's theory is still dependent on the validity of the Poisson-Boltzmann equations, so that, at best, it can only be used as a semi-empirical extension to the simple theory. It may also be shown that, if the theory is applied to unsymmetrically valent electrolytes, the statistical conditions of self-consistency fail completely. These conditions require that, in general, the ψ 's shall depend only upon the N 's and z 's according to the relation ¹

$$N_a \frac{\partial \bar{\psi}_a}{\partial z_\beta} = N_\beta \frac{\partial \bar{\psi}_\beta}{\partial z_a} \quad . \quad . \quad . \quad (343)$$

The Extended Theory of Scatchard.

A further objection to the extended theory put forward by Gronwall, La Mer and Sandved is apparent from the fact that

¹ L. Onsager, *Chem. Rev.*, **13** (1933), 73.

R. H. Fowler, "Statistical Mechanics" (1936), pp. 269, 551.

it takes no account of a change in the dielectric constant which may follow from the presence of ions in the solvent. Scatchard¹ points out that the lowering of the dielectric constant in the neighbourhood of an ion will not be the same as can be measured on a macroscopic scale, and that its change with concentration, as predicted from Wyman's work² makes it evident that the Debye constant κ^2 should not be proportional to the number of ions in unit volume of the solution, but to the number of ions in unit weight of the solvent (at constant temperature and pressure). With this modification, Debye's method may be used to calculate the terms in the non-ideal free energy expression, representing the charge-charge interactions and the "salting-out" effects. Finally, also, a term must be included to represent the non-electrolyte molecule-molecule interactions which is initially proportional to the concentration, but for which the slope decreases with increasing concentration.³ From these assumptions an expression may be obtained for the non-ideal free energy of the solution, if the distribution of the ions is supposed to be determined solely by the electrostatic interaction of their charges. The other thermodynamic properties of the solution, the osmotic coefficient and the logarithm of the activity coefficient, may then be calculated from the free energy. The expression for the heat of dilution involves taking the temperature derivatives of all the new parameters introduced into the free energy equation. It would not therefore be possible to extend the treatment to this property without introducing greater errors than the improved theory is intended to avoid.

The extended theory of Scatchard has, however, been applied to the osmotic coefficients of solutions of electrolytes with success, although the adjustable constants in his equation must themselves be computed by choosing them of such values as will make the theoretical curves fit the experimental results in one or two chosen cases. But, although it gives results which show good agreement with the best experimental work in the case of monatomic ions, the application

¹ G. Scatchard, *Chem. Rev.*, **19** (1936), 309.

² J. Wyman, *J. Amer. Chem. Soc.*, **58** (1936), 1482.

³ G. Scatchard, *Chem. Rev.*, **8** (1931), 321.

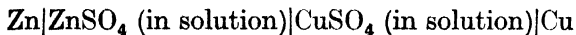
of the theory to polyatomic ions is considerably complicated by the fact that such ions cannot be assumed to be spherical—i.e., they will not have a definite ionic radius. Several fresh parameters must therefore be introduced in these cases, each one of which must be determined from the properties of the solutions. Nevertheless considerable progress has been made with the theory, both in its application to simple electrolytes and to the study of mixtures, and it appears to give a more satisfactory and generalised account of concentrated solutions of electrolytes than the theories of either Debye and Hückel, Gronwall and La Mer, or Bjerrum. Any generalised theory which accounts for the behaviour of strong electrolytes in solutions may be considered satisfactory so long as it can explain with some degree of success all the experimental work which has been done. For, the behaviour of electrolytes in strong solutions is so complicated, due to the many different forces and factors which contribute to the observed effects, that it is certain that present theories will fail to give a complete account of this behaviour, not so much because the physical conditions determining it are not known, but because the mathematical difficulties in deriving the complete solution of the equations have not yet been overcome. As each additional effect in the solutions is allowed for, in order to obtain a closer approximation to the true state of affairs in the solution, so do these difficulties increase and the problems of electrolyte solutions are therefore still very far from being solved.

CHAPTER VIII

THE THERMODYNAMICS OF ELECTRODE PROCESSES

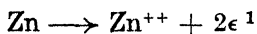
The Galvanic Cell.

IF two metals—for example, copper and zinc—are immersed in solutions containing their ions and the solutions are brought into contact in such a manner that mass diffusion is prevented (as in the Daniell cell), a potential difference is set up between the two metals, and it is therefore possible to draw electrical energy from the arrangement through an external circuit. Such a unit is known as a galvanic cell, and the electrical energy is obtained from it at the expense of a chemical reaction which proceeds in the cell. In the case of the Daniell cell this chemical reaction is the displacement of copper from the solution of its ions by zinc. Provided that complicating factors such as polarisation are avoided in the cell, so that the chemical reactions taking place are completely reversible, thermodynamic methods may then be applied to give a relation between the electrical energy obtained and the chemical energy expended by reaction. It is, however, first necessary to define, by convention, the sign of the E.M.F., and it has been agreed that the E.M.F. of the cell, represented diagrammatically thus :

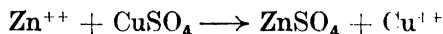


shall represent the tendency for a current to flow *inside the cell* from the left-hand electrode to the right electrode, as written. Regarding the cell as a source of current, therefore, the left-hand pole as written will be negative, the right-hand pole positive. Now, in the Daniell cell, before the zinc can replace the copper in the solution of its ions, it must itself pass into the ionic form, and in consequence the cell reaction is the overall effect deriving from two

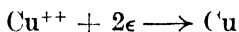
reactions one at each electrode, each of which involves an electron transfer. Zinc will therefore first ionise at the left-hand electrode



the zinc ions so formed passing into the copper sulphate solution, where, after diffusion through the membrane separating the two solutions, the reaction



takes place. The copper ions so liberated are then deposited on the copper electrode with the absorption of the two electrons liberated by the zinc



The net reaction is therefore

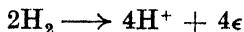


and if the cell and the electrode reactions have been written out correctly, the electrons appearing in the individual electrode reactions disappear in the cell reaction. In conformity with the convention laid down for defining the sign of the E.M.F. of a galvanic cell, the electrons have been passed inside the cell from left to right.

This principle of utilising the electrons liberated at the negative pole for the electrode reaction at the positive pole enables the electrode and cell reactions to be written down even though the galvanic cell represented may not be directly measurable in practice. In the water cell :

H_2 in contact with platinum	water rendered conducting with acid	oxygen in contact with platinum
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the hydrogen first ionises

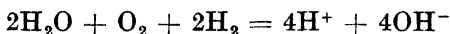


¹ This assumes that the zinc exists in the metal lattice in the non-ionised form. It is, however, almost certain from the crystal structure of metals that the ions are already present in the lattice, the extra electrons required to make the metal electrostatically neutral being incorporated in the lattice in such a manner as to allow them freedom of motion within the metal (Sommerfeld, *Ber.*, 61 (1928), 1171). This, however, will not affect the overall reaction, which involves only a transfer of electrons from one metal to the other.

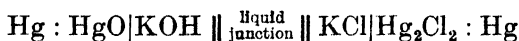
and the four liberated electrons enable the oxygen molecule to form hydroxyl ions at the anode :



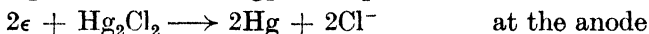
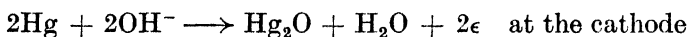
The net cell reaction is therefore



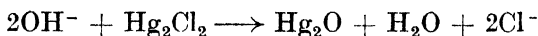
So also, in the more complicated cell



the electrode processes are :



and hence



is the overall reaction. The hydroxyl ions at the cathode are supplied from the potassium hydroxide solution and the chlorine ions appearing in the final reaction are liberated as such to the potassium chloride solution at the anode.

Heat Exchanges in the Galvanic Cell.

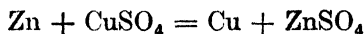
In the specific reaction



which may be made to take place in a Daniell type of cell, and thus to yield electrical energy, the heat evolved when the reaction is carried out under ordinary atmospheric conditions—i.e., at constant pressure so that the hydrogen is allowed to escape—is 39,390 calories, whereas if the reaction is carried out at constant volume in a sealed calorimeter, the heat change in the reaction is 37,730 calories. The difference between these two quantities of heat liberated may be accounted for by the external work done under constant pressure by the hydrogen liberated against the atmosphere. Thomsen,¹ first suggested that from the law of conservation of energy, the electrical energy obtained from such a reaction as the above when it is allowed to proceed in a cell should be exactly equivalent to the heat of reaction

¹ W. Thomsen, *Phil. Mag.*, 4 (ii) (1851), 429.

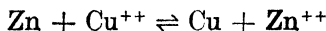
—i.e., to the decrease in the heat content of the system. For the reaction in the Daniell cell



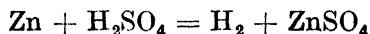
there is an evolution of heat equal to 50,130 calories, and since the E.M.F. of the cell is 1.09 volts, the electrical energy obtained from the reaction will be

$$\frac{2EF}{4.182} = \frac{2 \times 1.09 \times 96,495}{4.182} = 50,380 \text{ calories} \quad (344)$$

The factor 2 appears, since in the cell process



two gram electrons (faradays) are transferred from the zinc to the copper, and the factor 4.182 converts the units from joules to calories. The agreement in this case between the heat of reaction and the electrical energy obtained is very good, and appears to confirm Thomsen's view, but subsequent calculations¹ showed that the agreement in the case of the Daniell cell was quite a coincidence due (as will be seen later) to the fact that the E.M.F. of this cell has a negligible temperature coefficient. In the reaction



however, where the heat of reaction at constant pressure is 39,390 calories, the E.M.F. of the cell is 0.76 volt and the electrical energy obtainable is therefore only

$$2EF = \frac{2 \times 0.76 \times 96,495}{4.182} = 35,070 \quad . \quad (345)$$

It will be seen from (344) and (345) that there is a considerable difference between the electrical energy available from carrying out the reaction reversibly in the cell and the heat liberated by causing the reaction to proceed in a calorimeter. The difference can only be accounted for by supposing that heat has been absorbed during the working of the cell in overcoming external force.

Now, just as ΔA is a measure of the maximum work with

¹ Braun, *Wied. Annalen*, 17 (1882), 593.

volume and temperature chosen as independent variables, so ΔF represents the maximum work under the conditions implied by choosing pressure and temperature as variables with the volume constant (see p. 157). From the first law of thermodynamics it now follows that the electrical work obtainable from unit reaction¹ is conserved with the free energy change (maximum work) defined under these conditions—i.e.

$$zEF = \Delta F \quad . \quad . \quad . \quad . \quad . \quad (346)$$

Also from the first law, if ΔU represent the change in internal energy, considered positive if it increases,

$$\Delta H = \text{heat of reaction} = \Delta U - \Delta F$$

$$\text{or from (346)} \quad \Delta H = \Delta U - zEF \quad . \quad . \quad . \quad (347)$$

It is therefore evident that the heat of reaction does not represent the limiting quantity of work which may be obtained and the most efficient utilisation of a chemical reaction for the production of electrical energy does not consist in converting the heat into work. The difference between the heat of reaction and the electrical energy obtained represents the heat evolved or absorbed during the operation of the cell.

It is not therefore possible to check this difference directly and calorimetrically, but it may be tested with a fair degree of accuracy by applying the Gibbs-Helmholtz equation (157).² This equation applies only under conditions of thermodynamic reversibility. That a "thermodynamically reversible cell" is only a theoretical conjecture has already been explained (p. 154), but it has also been shown by Lewis that it is possible in practice to achieve conditions in a cell which approximate very closely to those of complete reversibility.³ In a process which is truly reversible in the thermodynamic sense the maximum work is obtained and by the Gibbs-Helmholtz equation (157)

¹ By unit reaction is meant the reaction in which the number of gram-moles involved is equal to the number appearing in the stoichiometric formulation of the reaction.

² Helmholtz, *Sitz. der Berlin Akad.*, 1 (1882), 22.

³ Lewis and Randall, "Thermodynamics" (1923), 113.

$$\Delta F + \Delta H = T \left(\frac{\partial \Delta F}{\partial T} \right)_P$$

$$\text{or from (346)} \quad \Delta H + zEF = TzF \left(\frac{\partial E}{\partial T} \right)_P \quad (348)$$

which with (347) gives

$$\Delta U = TzF \left(\frac{\partial E}{\partial T} \right)_P \quad (349)$$

From this equation the expression for the electrical energy obtainable from a chemical reaction carried out in a cell may be tested experimentally. In Table V, values for the various quantities are given, designed to verify the relation

TABLE V
Heat Measurements in some Galvanic Cells.

Cell.	E_{25}	$zEF =$ net work $= -\Delta F$ (calories).	$\Delta H =$ calori- metric heat evolved.	$\left(\frac{\partial E}{\partial T} \right)_P$	$TzF \left(\frac{\partial E}{\partial T} \right)_P$ = latent heat of working.	$zEF +$ ΔH .
Zn ZnSO ₄ CuSO ₄ Cu	1.0934	+ 50,395	- 55,189	- 4.3 × 10 ⁻⁴	- 5694	- 4794
Cu CuAc ₂ PbAc ₂ Pb ¹	0.4764	+ 21,960	- 16,500	+ 3.8 × 10 ⁻⁴	+ 4840	+ 5440
Hg Hg ₂ Cl ₂ ·KCl KOH·Hg ₂ O Hg ¹	0.1483	+ 7,570	+ 3,180	+ 8.4 × 10 ⁻⁴	+ 11,280	+ 10,850
Pb PbCl ₂ Hg ₂ Cl ₂ Hg ¹	0.5357	+ 23,320	- 22,730	+ 1.45 × 10 ⁻⁴	+ 1,990	+ 591
Zn ² amal. ZnSO ₄ ·7H ₂ O HgSO ₄ Hg ¹	1.4324	+ 66,100	- 81,127	+ 11.9 × 10 ⁻⁴	- 15,820	- 15,027

¹ H. Jahn, *Wied. Annalen*, **50** (1893), 189.

² Bugersky, *Z. anorg. Chem.*, **16** (1891), 140.

³ Data taken from Lewis and Randall, "Thermodynamics" (1923), p. 171.

⁴ Cohen, *Z. physikal. Chem.*, **60** (1907), 706.

for a number of cells. The figures in the last two columns should, by the Gibbs-Helmholtz equation, agree, but the discrepancies may be attributed, in part at least, to the difficulties in determining accurately by experiment the temperature coefficient of the E.M.F. and the calorimetric heat ΔH evolved. The values of $zEF + \Delta H$ moreover represent the difference of two large quantities, and small errors in either of these will therefore increase the relative error in the final quantity. In the third cell reaction—that of caustic potash with mercuric chloride—heat is absorbed during the chemical process, whereas there is a definite

positive E.M.F., a fact accounted for by the large temperature coefficient of this cell. This more than counterbalances the deficit of heat absorbed, and the excess is then available for conversion into electrical energy. In the reactions for the Daniell cell and the lead-mercurous chloride cell, the differences between the figures in the last two columns are particularly large, but the measurements of the calorimetric heat values in these cases present considerable difficulties.

In the cases of all these cells, however, it is important to realise that the electrical energy obtained is a consequence of the chemical reaction which goes on in the cell, and that it is in no way a property of the cell itself. The thermodynamic treatment following the application of the Gibbs-Helmholtz equation has emphasised this fact, and the reversible cell is no more than a useful arrangement whereby the conversion of chemical into electrical energy may be effected without any loss of efficiency. Only when the conditions are reversible, however, is the maximum work obtained.

Chemical Equilibria in Galvanic Cells.

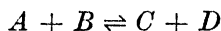
During the earlier part of the nineteenth century a large mass of thermochemical data was compiled in the belief that the heat of reaction was in some way connected with the affinity of the reaction, which was supposed to be the "tendency of the reaction to take place." The affinity defines, however, the direction and extent to which a chemical reaction proceeds towards its equilibrium, but it is in no way concerned with the speed of the reaction. Since the change of free energy, which is the net work required (or obtained) for the reaction to proceed to equilibrium, is a measure of the tendency towards spontaneous change, this function will give a quantitative significance to the affinity of a reaction.

From equation (150) we have, at constant pressure,

$$\left(\frac{\partial F}{\partial T}\right)_P = -S$$

implying that in every spontaneous change the free energy must tend to decrease to a minimum until, at equilibrium when the entropy reaches a maximum, $\partial F = 0$.

The value of the net work, of which ΔF is a measure, has already been found for a simple chemical reaction,



by an application of the van 't Hoff "equilibrium box" method (see p. 158). If we express the concentrations of the gaseous reactants and products in the reaction, by their corresponding partial pressures, we have :

$$\begin{aligned}\Delta F &= RT \ln \frac{p_c(C)p_c(D)}{p_c(A)p_c(B)} - RT \ln \frac{p_r(C)p_r(D)}{p_i(A)p_i(B)} \\ \Delta F &= RT \ln K_p - RT \Sigma_v \ln p \quad . \quad . \quad . \quad (350)\end{aligned}$$

using the same notation as before.

Since equation (350) expresses the active masses of the relevant species as partial pressures and not as activities, it will give the maximum work only over the limiting range of pressures to which the simple gas laws may be applied without sensible error. At equilibrium, since

$$\begin{aligned}\Delta F &= 0 \\ \Sigma_v \ln p &= K_p \quad . \quad . \quad . \quad (351)\end{aligned}$$

and no work is done or obtained in passing from one side of the equilibrium to the other. This is a natural consequence, moreover, of the entropy being here a maximum; for between any two points within a system where the entropy is everywhere a maximum, no work can be done or obtained in passing from one point to the other. If the reactants are chosen at unit concentration on the pressure scale, and the products are brought to the same unit concentration,

$$RT \Sigma_v \ln p = 0 \quad . \quad . \quad . \quad (352)$$

and

$$\Delta F = RT \ln K_p \quad . \quad . \quad (353)$$

Equation (353) may be tested experimentally by measurements of the E.M.F. of a cell in which the reaction is allowed to proceed as nearly as possible reversibly, by opposing the E.M.F. of the cell with an equal and opposite potential difference. If, then, the applied E.M.F. necessary

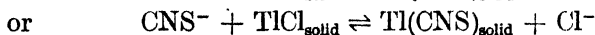
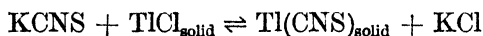
to bring the whole reaction system to equilibrium be E , we have from (346)

$$\Delta F = zEF$$

and, in general,

$$zEF = RT \ln K \quad . \quad . \quad . \quad (354)$$

The practical difficulty experienced in such measurements lies, however, in the choice of a suitable cell in which the equilibrium of the reaction taking place is not too far over on either side. Knüppfer¹ found that the reaction,



was quite suitable for experimental investigation. By applying the van 't Hoff isotherm to this reaction proceeding in the forward sense, we have :

$$zEF = RT \ln \frac{[\text{Cl}^-]_e}{[\text{CNS}^-]_e} - RT \ln \frac{[\text{Cl}^-]}{[\text{CNS}^-]} \quad (355)$$

The active masses of the solid precipitated thallium sulphocyanide and chloride are constant, and do not therefore appear in the isotherm equation. The reaction may be made to take place in a galvanic cell of the type,



Knüppfer set up an arrangement of the type illustrated in Fig. 64 consisting of two half-cells, one having a solution of potassium chloride saturated with thallium chloride, the other having potassium sulphocyanide saturated with the thallium salt. The liquid junction between the two halves was established through a bridge of saturated potassium chloride solution. Fused-in platinum wires were connected to the potentiometer through mercury. In order to determine the equilibrium constant, Knüppfer made

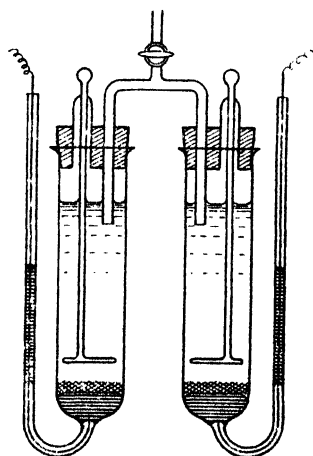
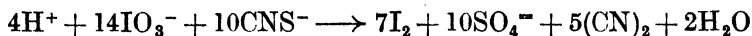


FIG. 64.—KNÜPPFER'S CELL.

¹ Knüppfer, *Z. physikal. Chem.*, 26 (1898), 255.

a total analysis of the sulphocyanide and chloride ions, followed by a determination of the sulphocyanide only, present as the potassium salt, using the reaction



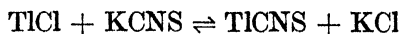
This gave a measure of the chloride ion concentration by difference, and hence of the ratio Cl^-/CNS^- . The arbitrary ratio of the chloride to the sulphocyanide ion was chosen to be 0.83, very near to the equilibrium constant at 39.9°C ., one of the temperatures at which measurements were made. The E.M.F. at this temperature was therefore very small, since the concentration terms in the isotherm equation were then almost equal. Some of Knüppfer's results are exhibited in Table VI, where a comparison of the measured E.M.F.'s

TABLE VI.

Measurements on Knüppfer's Cell.

Temperature.	<i>K</i> found.	Ratio.	<i>E</i> found.	<i>E</i> calculated.
39.9° C.	0.85	0.83	0.0010	0.0006
		1.50	— 0.0140	— 0.0153
20.0° C.	1.24	0.84	0.0105	0.0098
		1.52	— 0.0048	— 0.0052
0.8° C.	1.74	0.84	0.0175	0.0171
		1.55	0.0037	0.0027

and those calculated from the isotherm equation gives an indication of the accuracy to which the theoretical equation has been verified. The method is undoubtedly the simplest by which the van 't Hoff isotherm may be tested experimentally, and although the agreement obtained by Knüppfer is not very striking, it is satisfactory when the experimental difficulties of the analyses and measurements are remembered. A calculation of the temperature coefficient of the equilibrium constant for the cell reaction,



was also made by Knüppfer from the integrated form of equation (172) *i.e.*,

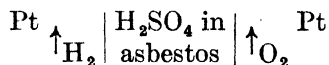
$$\ln K_2 - \ln K_1 = \frac{\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad (356)$$

The temperature coefficient of the E.M.F. was also determined in a similar manner. The agreement found between the calculated and experimental values of $K_{20}/K_{39.9}$ and $K_{0.8}/K_{39.9}$ was of the same order as that for the E.M.F.'s

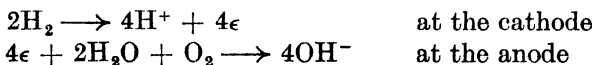
The Calculation of Equilibrium Constants from Electrical Measurements.

The process of determining the E.M.F. due to a given reaction proceeding in a cell by an application of thermodynamic principles may be reversed and the equilibrium constant of a chemical reaction computed from measurements of the maximum electrical energy obtained from the reaction by means of a reversible cell. The method is particularly suitable in those cases where otherwise no value could be found for the equilibrium constant at ordinary temperatures.

Such a reaction, for example, is that of the synthesis of water for which, at ordinary temperatures, the equilibrium is so very much on the side of the water that no direct measurement of the position of the equilibrium is possible. The reaction may, however, be made to take place as nearly as possible reversibly, as in the Mond-Langer cell¹ (see p. 244)



where the electrode reactions are :



and the overall reaction for the passage of four faradays of electricity is therefore the synthesis of 2 gram-molecules of water. The isotherm equation (354) for this synthesis is

$$4EF = RT \ln \frac{p_{\epsilon}[\text{H}_2\text{O}]^2}{p_{\epsilon}[\text{H}_2]^2 p_{\epsilon}[\text{O}_2]} - RT \ln \frac{p[\text{H}_2\text{O}]^2}{p[\text{H}_2]^2 p[\text{O}_2]} \quad (357)$$

the second term corresponding to the pressures of the three components in the cell the E.M.F. of which is to be measured. The E.M.F. of the cell is given by Mond and Langer as 1.15

¹ Mond and Langer, *Proc. Roy. Soc., A*, 46 (1889), 296.

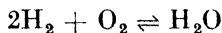
volts at room temperature (15°C.), so that, since $\frac{RT}{F} \log_e 10$ is approximately equal to 0.058 joule, equation (247) becomes:

$$1.15 = \frac{0.058}{4} \log_{10} K_p - \frac{0.058}{4} \log_{10} \frac{p(\text{H}_2\text{O})^2}{p[\text{H}_2]^2 p[\text{O}_2]}. \quad (358)$$

In the cell, the partial pressure of water is equal to its saturation vapour pressure at the room temperature (15°C.)—i.e., is equal to 0.015 atmosphere, and the pressures of hydrogen and oxygen are each equal to 1 atmosphere, since they are being slowly bubbled past platinum at this pressure. Thus from (358)

$$1.15 = \frac{0.058}{4} \log_{10} K_p - \frac{0.058}{2} \log_{10} 0.015. \quad (359)$$

At room temperature for the forward reaction



K_p , the equilibrium constant, is therefore approximately equal to 10^{75} . Further, from a knowledge of the heat of reaction it is possible to calculate the values of the equilibrium constant at any other temperature by substituting this in the isotherm, and so to determine the position of the equilibrium for the dissociation of steam at high temperatures. But the values so obtained are not in good agreement with the experimental results of Nernst and von Wartenburg.¹ This may be due to the fact that the value 1.15 volts for the E.M.F. of the Mond-Langer cell, even with the most carefully platinised electrodes, does not represent the reversible E.M.F. of the water cell, due to upon the formation of oxide films on the surface of the platinum electrodes.²

A similar example in which the equilibrium could only be determined by an indirect method, is that of the

¹ Nernst and von Wartenburg, *Nacht. Kgl. Ges. Wiss. Göttingen* (1905), 35; *Z. physikal Chem.*, 56 (1906), 534.

von Wartenburg, *ibid.*, 54 (1906), 513.

Compare with Brönsted's indirect method, *ibid.*, 65 (1909), 84, 744.

² T. P. Hoar, *Proc. Roy. Soc., A*, 143 (1934), 628.

dissociations of metallic oxides. These may be studied from measurements on such cells as



the E.M.F., E , of which is exactly the same as that of the hydrogen-oxygen cell in which the partial pressure of oxygen is that pressure in equilibrium with lead oxide at the temperature of measurement—*i.e.*, is equal to the dissociation pressure of the oxygen in the reaction



The measured E.M.F., E_1 of the first of these cells is 0.247 volt, and E_2 , that of the hydrogen-oxygen cell calculated from measurements at high temperatures, is 1.227 volts at 25° C.¹ This value, obtained indirectly, eliminates therefore the errors in the direct measurements arising from the irreversibility of the oxygen electrode (see p. 274)—the extent of this irreversibility decreases with increasing temperature, probably due to the dissociation of the metallic oxides which give rise to it. The difference between these two E.M.F.'s is equivalent to that of the concentration cell

O_2 , at diss. press. of $\text{PbO} | \text{KOH} | \text{O}_2$, at atm. pressure

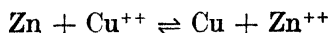
$$\text{i.e.,} \quad E_2 - E_1 = \frac{RT}{4F} \ln \frac{p_{\text{diss.}} [\text{O}_2]}{p_{\text{atms.}} [\text{O}_2]} \quad . \quad . \quad . \quad (360)$$

$$\text{or} \quad 1.226 - 0.247 = 0.0145 \log_{10} p_{\text{diss.}} [\text{O}_2] \quad . \quad . \quad (361)$$

$$\text{or} \quad p_{\text{diss.}} [\text{O}_2] = 4.2 \times 10^{-17} \text{ atmosphere} \quad . \quad (362)$$

As with the reaction representing the dissociation of water, the dissociation pressures of lead oxide at higher pressure temperatures may be calculated from a knowledge of the heat of the reaction.

A final example of this method of using the isotherm in conjunction with E.M.F. measurements for the determination of inaccessible equilibria, may be quoted from the Daniell cell reaction,



for this reaction, equation (354) becomes

$$E = 1.09 = \frac{RT}{2F} \ln \frac{[\text{Zn}^{++}]_e}{[\text{Cu}^{++}]_e} - \frac{RT}{2F} \ln \frac{[\text{Zn}^{++}]}{[\text{Cu}^{++}]} \quad . \quad (363)$$

¹ Lewis and Randall, *J. Amer. Chem. Soc.*, 36 (1914), 1969.

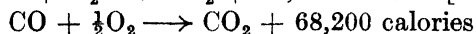
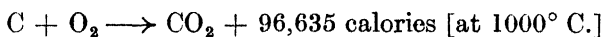
The concentration terms $[Zn^{++}]$ and $[Cu^{++}]$ in the final term here represent, respectively, the initial concentration of the zinc ions and the final concentration of the copper ions in the displacement reaction. The value found for the ratio of the equilibria concentrations of zinc and copper in the solution is

$$\frac{[Zn^{++}]_e}{[Cu^{++}]_e} = 10^{37}$$

illustrating the remarkable degree of completeness with which zinc replaces copper from its solutions at room temperatures. Such a computation of the position of equilibrium could certainly never be made at room temperatures by any direct method involving analytical methods at present available for the estimation of small quantities of copper present in solution when a large quantity of zinc is also present.

Fuel Cells.

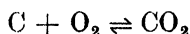
The thermodynamic principles which have been applied to the problem of the galvanic cell show that any chemical reaction which can be caused to take place in a cell may be used as a source of electrical energy. It is not surprising, therefore, that many attempts should have been made to direct the world's main fuel sources with a view to obtaining electrical energy cheaply. If such reactions as



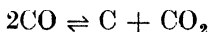
which involve the burning of cheap material like coal accompanied by a very large liberation of thermal energy, could be made to take place in a cell, very large supplies of electrical energy would be made available. One kilogram of coal would, if all its energy became available, give 8940 ampère hours, but, utilised in the ordinary way by first turning water into steam and subsequently using this to drive a dynamo, the maximum energy obtained never exceeds 1 kilowatt-hour in the most efficient system.

The value of the E.M.F. which could be obtained from such reactions if the whole of the energy could be utilised

electrically, may be calculated theoretically, provided the equilibrium constant of the reaction is known. For the reaction



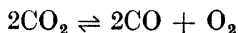
this equilibrium constant K_p is not directly determinable, for the equilibrium is far over on the right-hand side, but it may be calculated from the constants for two other reactions—viz., the dissociation reactions of carbon monoxide and carbon dioxide. For the carbon monoxide reaction



at 1300°K. , the partial pressures of the two gases are $p[\text{CO}_2] = 0.0075$ and $p[\text{CO}] = 0.9925$ —i.e., the equilibrium constant is :

$$K_1 = \frac{p[\text{CO}]^2}{[\text{C}_{\text{solid}}]p[\text{CO}_2]} = \frac{(0.9925)^2}{0.0075} = 131 \quad . \quad (364)$$

The active mass of the solid carbon is constant, and it is therefore omitted from the equilibrium equation. For the carbon dioxide dissociation,



the equilibrium constant K_2 is found to be 3.7×10^{-4} at this same temperature and therefore

$$\frac{K_1}{K_2} = \frac{p[\text{CO}]^2}{p[\text{CO}_2]} \cdot \frac{p[\text{CO}_2]^2}{p[\text{CO}]^2 p[\text{O}_2]} = \frac{p[\text{CO}_2]}{p[\text{O}_2]} = K_p = 4 \times 10^5 \quad (365)$$

The E.M.F. obtainable from the reaction if this could be made to take place in a cell, perfectly efficiently, may now be found from the van 't Hoff isotherm (354) :

$$RT \ln K_p = zEF$$

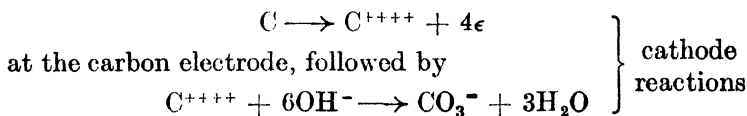
where E is the E.M.F. given by the cell. z , the number of faradays involved in unit reaction, is for this particular reaction 4, since carbon is tetravalent, and therefore requires the passage of four faradays per gram-atom for its complete combustion in the cell. Hence from (354) and (365) we have, at 1300°K. :

$$E = \frac{RT \ln K_p}{2F} = \frac{2 \times 1,300 \times \ln K_p}{4 \times 96,540} = 1.05 \text{ volts.} \quad (366)$$

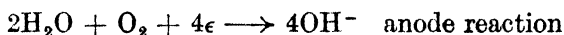
In this particular reaction the absolute temperature and the equilibrium constant vary in opposite senses to almost equal extents, and so the E.M.F. calculated at room temperatures—viz. 1.01 volts—does not differ very greatly from that at high temperatures—viz., 1.05 volts at 1,300° K.

(a) *Jacques' Carbon Cell.*

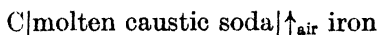
Any cell in which such a combustion process is to take place in order to obtain electrical energy must involve some such series of reactions as the following :



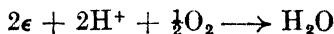
and using the electrons liberated at the cathode in the anode reaction :



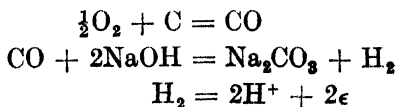
Jacques¹ attempted to use these reactions in a cell consisting of electrodes of battery carbon and iron around which air flowed, in molten caustic soda as electrolyte :



the E.M.F. being just over 1 volt. Haber² pointed out that, owing to the iron becoming rapidly passive, this electrode begins after some time, to operate essentially as an air electrode, and the presence of small quantities of manganese which always accompany the iron, in the melt, facilitates this reaction :



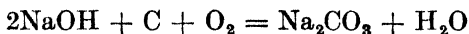
probably by the alternate formation and reduction of the MnO_4^- ion. At the carbon electrode the reactions are :



¹ A much more detailed account of the various fuel cells which have been designed is given by Allmand and Ellingham, "Applied Electrochemistry" (1924), p. 217.

² Haber and Bruner, *Z. Electrochem.*, 10 (1904), 697; 12 (1906), 78.

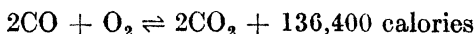
so that the total reaction taking place in the cell is :



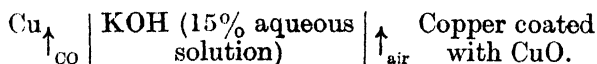
the E.M.F. being that of a hydrogen-oxygen cell operating under the given conditions. The large quantities of coal which must be used to keep the cell hot, and the rate (some litres per minute) at which air must be passed over the iron electrode to prevent polarisation, render the cell economically impossible for the production of electrical energy at a cost which will compete with other methods.

(b) *Hofmann's Carbon Cell.*

A somewhat different cell was set up by Hofmann,¹ in which it was proposed, by using carbon monoxide as the initial substance, to overcome the difficulties attendant upon the use of carbon, and to direct the chemical energy of the reaction



into electrical energy. The gases which were used at the electrodes were therefore carbon monoxide which was streamed past metallic copper (where it is absorbed) and, on the other side, air passed round a copper electrode coated with cupric oxide. As cell electrolyte, a 15% aqueous solution of caustic potash was recommended by Hofmann :



The cell gives an E.M.F. of 1.04 volts, but suffers from the disadvantage of polarisation, to which many of these gas cells are open. The only effective method of preventing polarisation would have been to blow the gases over the electrodes very rapidly, and such a process immediately ends the practical utility of the cell due to the prohibitive cost which would be incurred on a large scale.

(c) *Haber's Fuel Cell.*

Haber had previously overcome the difficulty of polarisation in the carbon monoxide-oxygen cell to some extent,

¹ Hofmann, *Ber.*, 51 (1918), 1521; 53 (B) (1920), 914.

Hofmann and Wurthmann, *ibid.*, 52 (B) (1919), 1185.

by making use of the fact that glass, heated almost to melting, becomes a good conductor of electricity.¹ If glass vessels formed by sealing off equal lengths of glass tubing at one end were platinised inside and outside, to make the two surfaces into electrodes, and the gases were streamed past these (Fig. 65), then at high temperatures, just below the melting point of the glass, the glass tubing between the electrode surfaces functioned as the cell electrolyte, and the combustion of carbon monoxide within the cell, provided electrical energy. Like the sodium hydroxide

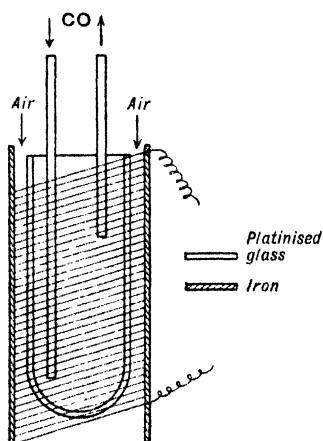


FIG. 65.—HABER-MOSER GLASS CELL (diagrammatic).

cell of Jacques, however, the large quantities of heat which must be expended to make the glass a conductor, place the cell beyond the requirements of practical and economic utility.

(d) *The Mond-Langer Hydrogen-Oxygen Cell.*

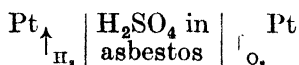
The most successful attempt to produce a gas battery which would be economically useful, was made by Ludwig Mond and Langer who emphasised the importance of maintaining unimpaired the condensing power of an absorbent for the electrode

gases.² Following Grove's suggestion, their cell used the water synthesis reaction in place of any of the carbon combustion reactions. Platinum black, "the most suitable absorbent for gas batteries," was found rapidly to lose its condensing power when it became wet. This placed all attempts to use liquid electrolytes under an initial disadvantage. Far more successful was the use of an electrolyte soaked up in some porous material after the manner adopted in dry batteries. The condition of reversibility which, as former attempts to set up fuel cells had

¹ Haber and Moser, *Z. Electrochem.*, **11** (1905), 593.

² Mond and Langer, *Proc. Roy. Soc., A*, **46** (1889), 296.

shown, was so important for the successful operation of the cell, could be assured only if the gas was supplied to the electrode as quickly as it became ionised. The current density therefore had to be exceedingly low, and the gases were arranged to diffuse through only a short distance before they reached the surface where ionisation took place. The arrangement



fulfilled these conditions and was practicable, since it was only necessary to impregnate a diaphragm of asbestos with dilute sulphuric acid to form the electrolyte, and to cover this on both sides with thin leaves of platinum or gold coated with a film of platinum black to serve as electrodes. At intervals these electrodes were attached to some good conductor such as copper or lead, designed to reduce the internal resistance of the cell, and the diaphragms so constructed were piled in frames in such a manner that gas could be passed through a whole series of cells, hydrogen on one side and oxygen on the other. Paraffin was poured over the platinum leaf at the points of contact of the copper wires used to lead off the current, so that corrosion was prevented.

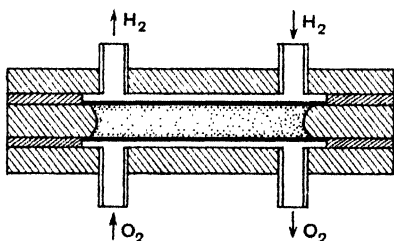


FIG. 66.—MOND-LANGER FUEL CELL.

With this experimental arrangement, the maximum E.M.F. which was obtained with the best platinised electrodes never exceeded 0.97 volt,¹ whereas the theoretical value of the E.M.F. for the hydrogen-oxygen cell in which all the chemical energy is converted into electrical energy is 1.227 volts. The difference, it has been suggested, is due to the formation of oxides of platinum at the electrodes, which prevent its saturation with oxygen.² At high temperatures,

¹ Compare Richards' value 0.979 volt, *J. Physical Chem.*, **32** (1928), 990.

² Richards, *loc. cit.*

F. P. Bowden, *Proc. Roy. Soc., A*, **125** (1929), 446.

where these oxides would be dissociated, the theoretical value of the E.M.F. is approached.¹ The transport of the sulphate ion from the oxygen to the hydrogen electrode results in the acid becoming gradually weaker on one side and stronger on the other, so that after operating for some time the cell begins to show the characteristics of concentration polarisation. This, however, may be minimised by reversing the gases passing over the electrodes at intervals. Using sodium chloride as an electrolyte in place of sulphuric acid, the observed E.M.F. is 0.86 volt, as against the calculated value 1.47 volts, and the difference, 0.61 volt, is almost entirely accounted for by the observed polarisation E.M.F. of 0.54 volt. Economic considerations, however, again rule out the possibility of using the cell in competition with other methods of producing electrical energy, for the initial cost of the cell is high, and the platinum black which is the essential feature of the electrodes, is very susceptible to traces of impurity such as carbon monoxide, which might be present in hydrogen obtained, for instance, by the water-gas reaction.

Theory of the Galvanic Cell—Nernst's Theory of Solution Pressures.

In the preceding considerations of the galvanic cell, the E.M.F. has been related to the actual chemical reaction proceeding in the cell, but nothing has been said about the seat of the E.M.F. The thermodynamic treatment of the problem, while giving a statement of the result, is incapable of giving any details about the mechanism whereby the E.M.F. is set up, and other considerations have to be introduced in order to obtain information about this. Considerable confusion has arisen until recently, since, in making a measurement of the E.M.F. of a cell, not only are the potential differences in the cell itself being measured, but so also is the metal-metal contact potential in the external circuit. It is well known that in a homogeneous conductor a potential difference cannot exist permanently between two points, for a current will immediately flow until

¹ Haber, *Z. anorg. Chem.*, 51 (1906), 245, 289, 356.

the potential difference is reduced to zero. The electrical energy of a cell cannot therefore derive entirely from conditions existing within the metals of the electrodes nor in the body of the solution, but this energy must have its origin in the phase boundaries of the cell. The total E.M.F. measured will therefore be the overall result of specific conditions obtaining at the metal-metal junction in the external circuit and at the metal-solution and the liquid-liquid interfaces in the cell. For many years the metal-metal junction potential was not regarded as of any importance among these quantities, since the simple application of thermodynamics to the chemical reaction taking place in the cell enabled a relation to be derived, for the electrical energy produced, in terms of the energy of the chemical reaction. Moreover, experimental measurements confirmed this expression for the E.M.F.'s of reversible cells. The existence of contact potentials between two metals, of the same order as the E.M.F.'s observed in cells, was therefore ascribed to atmospheric action or to the existence of a film of moisture at the metal junction.¹ As evidence for this view the Volta series was found to correspond closely to the series obtained by setting the metals in order of their heats of oxidation.²

Nernst in 1889 put forward his theory of solution pressure to explain the origin of the E.M.F. in terms of effects taking place at the surfaces of the electrodes. He supposed a metal immersed in a solution to lose ions to the solution in a manner analogous to that in which a solvent separated from a solution by a semi-permeable membrane will pass its molecules into the solution until the pressure set up just opposes the osmotic pressure.³ If the metal is immersed in a solution of its own ions, the passage of the ions from the lattice to the solution by reason of the metal's solution pressure will be opposed by the osmotic pressure of the ions

¹ Fairly accurate recent measurements of the Volta potentials and the E.M.F.s of the corresponding cells have confirmed the earlier conclusions on the relative magnitudes of these quantities (W. D. Bancroft and J. D. Porter, *J. Physical Chem.*, **40** (1936), 1201).

² O Lodge, *Phil. Mag.*, **49** (v) (1900), 35.

³ W. Nernst, *Z. physikal. Chem.*, **4** (1889), 129.

in the solution, and this process can proceed only so long as the solution pressure exceeds the osmotic pressure. In this case the metal will be left with a net negative charge, and at equilibrium the potential set up is in the direction solution to metal. But if the osmotic pressure of ions in the solution exceeds the solution pressure, ions are deposited on the metal surface and the potential difference is in the direction metal to solution. The state of affairs at the interface is therefore characterised by the existence, parallel with and next to the metal surface, of two layers, one of negative charges left on the metal, the other of positive charges (ions) attracted back to this negative charge on the metal. Whichever layer is positively charged depends on the relative magnitude of the osmotic and the solution pressures, since the first process may accordingly be one of deposition or solution of positive ions. In either case there is set up a double layer of the type postulated by Lippmann¹ and Helmholtz² in their explanation of the action of the capillary electrometer. The intensity of the electrostatic field set up by the double layer may then be supposed to retard the further loss of metal ions from the lattice.

An expression for the electrode potential of an electrode relative to a solution of its ions in which it is immersed may be found from the expression for the free energy in terms of the activities. For if the potential difference is in the direction metal to solution—*i.e.*, if on Nernst's theory, the osmotic pressure P of the solution exceeds the solution pressure p of the metal—the partial molar free energy of the ions within the metal where their activity is a_s , measured from the standard free energy $\bar{F}^\circ$, will be given by equation (177)

$$\bar{F}_s - \bar{F}^\circ = RT \ln a_s \quad . \quad . \quad . \quad (367)$$

and for the ions in the solution at activity a_1 their partial molar free energy measured from $\bar{F}^\circ$ will be :

$$\bar{F}_1 - \bar{F}^\circ = RT \ln a_1 \quad . \quad . \quad . \quad (368)$$

¹ Lippmann, *Pogg. Annalen*, **149** (1873), 547.; *Wied. Annalen*, **11** (1880), 316.

² Helmholtz, *Helmholtz Ges. Abh.*, **1**, 925.

The difference between the two partial molar free energies of the ions in the metal and in the solution which will be independent of the common standard free energy $\bar{F}^\circ$ from which each has been measured, will therefore be :

$$(\bar{F}_s - \bar{F}_0) - (\bar{F}_1 - \bar{F}^\circ) = + \Delta \bar{F} = RT \ln \frac{a_1}{a_s} \quad (369)$$

Also, since this difference in free energy is by equation (346) equal to the electrical work obtained zEF

$$+ \Delta \bar{F} = zEF = RT \ln \frac{a_1}{a_s} \quad . \quad . \quad (370)$$

$$\text{or} \quad E = \frac{RT}{zF} \ln \frac{a_1}{a_s} \quad . \quad . \quad . \quad (371)$$

An alternative method given below of arriving at this result, using the assumptions of the Nernst solution pressure theory, has the disadvantage of being open to criticisms which have been brought against the theory, but it illustrates the method of carrying out an isothermal reversible cycle on the system. If it be supposed, for example, that δx gram of the metal is transferred from the metal to the solution under conditions of thermodynamic reversibility—*i.e.*, such that the system is at every stage only infinitesimally removed from equilibrium, then $zF\delta x$ will represent the number of coulombs which pass during the transference, z being the valency of the ion: the work done on the system is therefore $zEF\delta x$. To return the system to its former state, the δx gram of the ion which has been transferred from the metal to the solution, must be removed from the solution, a process involving no work, and compressed from the osmotic pressure P to the solution pressure p , requiring an amount of work $\delta x RT \ln p/P$ to be done. Finally the δx gram of the metal may be returned to the metal without any further change in the work term. The total work done in such an isothermal reversible cycle is zero, for otherwise it would be possible to obtain work from a system all at one temperature, and this is precluded by the second law.

$$\text{Hence} \quad \delta x RT \ln \frac{p}{P} + \delta x zEF = 0 \quad . \quad . \quad (372)$$

$$\text{and} \quad E = \frac{RT}{zF} \ln \frac{P}{p} \quad . \quad . \quad . \quad (373)$$

In the derivation of this expression it has been assumed that the system is sufficiently dilute for the gas laws to be applied, but the formula may be made to hold at all concentrations by replacing the pressure terms by the corresponding activities—*i.e.*, assuming that the solution pressure can be replaced by an activity, we have :

$$E = \frac{RT}{2F} \ln \frac{a_1}{a_s} \quad . \quad . \quad . \quad (374)$$

which is identical with (371) obtained by free energy considerations.

The active mass of the ions in the metal is constant, and the term $\frac{RT}{2F} \ln a_1$ may therefore be replaced by E^0 —*i.e.* :

$$E = E^0 - \frac{RT}{2F} \ln a_s \quad . \quad . \quad . \quad (375)$$

Thus for the half reaction,



the single potential is given by

$$E = E^0 - \frac{RT}{F} \ln \frac{(\text{Fe}^{+++})}{(\text{Fe}^{++})} \quad . \quad . \quad . \quad (376)$$

z in this case being unity, since only one faraday is liberated for unit reaction. The quantity E^0 in this expression is called the normal or standard potential of the electrode, since $E = E^0$ when the electrode is in contact with a solution of its own ions at unit activity. Its determination can, however, only be made by choosing some arbitrary standard from which it is agreed to measure all electrode potentials, for the determination of the absolute potential of a single electrode has not proved a practicable possibility.¹ As will be seen later, any attempts to determine the absolute zero of potential are doomed to failure, due to the fact that the metal-metal contact potential in the outer circuit is as important a factor in determining the E.M.F. of a cell as the liquid-electrode interfaces (see p. 259). Since the change in free energy in an electrode process is equal to

¹ For attempts to determine the absolute potential of an electrode, see for example M. Andauer, *Z. Physikal. Chem.*, **125** (1927), 135.

Billitzer, *Trans. Amer. Electrochem. Soc.* (1930).

+ zEF , so for the standard change in partial molar free energy in the same process we have from (354)

$$zE^0F = \Delta F^0$$

and the values of this for two half-cells when combined will give the standard free energy for the cell reaction.

If two similar electrodes each in contact with a solution of its own ions, the one solution having a mean activity $a_{\pm}'$ the other a mean activity $a_{\pm}''$, are connected together through an external circuit and the cell is completed by a liquid bridge of saturated potassium chloride (see p. 277), the total E.M.F. of the cell, ignoring the effect of the liquid junction, will from (375) and (199) be :

$$\begin{aligned} E &= (E_1 - E^0) - (E_2 - E^0) \\ &= \frac{RT}{zF} \ln a_{+}'' a_{-}'' - \frac{RT}{zF} \ln a_{+}' a_{-}' \end{aligned} \quad (377)$$

$$\text{or} \quad E = \frac{2RT}{zF} \ln \frac{a_{\pm}''}{a_{\pm}'} \quad . \quad . \quad . \quad (378)$$

This expression might also have been derived by carrying out an isothermal reversible cycle on the concentration cell between its two concentration limits.

Theory of the Diffuse Double Layer (Gouy).

The conception of the electric double layer as proposed by Helmholtz and applied to the case of a metal dipping into a solution of its own ions by Nernst, involved no detailed consideration of the mechanism whereby the charged ions were kept separated at a small but finite distance from the oppositely charged surface. Moreover, calculations from Helmholtz's equation of the apparent electric moment of the adsorbed molecules show variations of this with concentration, and it is therefore necessary for the concept of a rigid double layer to be replaced by one of a boundary layer, the structure of which can change with concentration. The simple view of the double layer has therefore been modified, and it is supposed to have a thickness equal to that of several molecules, which will account for the separation of the charges. These charges are not supposed to

reside on the surface of the metal, but are considered to be associated with the ions in the double layer, and therefore to be distributed throughout the whole of the region in the neighbourhood of the interface. Thermal agitation will so influence them that they could not retain their positions in immediate proximity to the metal surface¹ (Gouy).

As the metal surface is approached from the solution, therefore, the symmetrical distribution of positive and negative ions gives place to an increased concentration of ions of one sign and a decreased concentration of those of the opposite sign, the osmotic forces so set up being balanced at every point by the electric force due to the potential gradient. From the concept of a diffuse double layer we see that this will be similar in structure to the ion atmosphere round an ion in solution, and it should therefore be possible by an application of Debye and Hückel's method, to obtain an estimate of the nature and of the effective thickness of the layer. For this calculation we shall choose as our standard zero of potential the main body of the solution where the asymmetric ionic distributions in the neighbourhood of the electrode surface have disappeared. The potential of the electrode may then be defined against this arbitrary zero of potential. If therefore at any point in the body of the solution where the potential is zero, the positive ion density be n_0 , and at a point where the potential in the double layer is $\bar{\psi}$, it be n_+ , these ion densities are related by the Boltzmann equation, provided the solution is sufficiently dilute for the simple analysis to be applied—i.e.

$$n_+ = n_0 \exp. \left(- \frac{e\bar{\psi}}{kT} \right) \quad . \quad . \quad . \quad (379)$$

In (379) k is the Boltzmann constant and $e\bar{\psi}$ (the product of the ionic charge and the potential) is the energy of each ion. So also for the negative ions,

$$n_- = n_0 \exp. \left(+ \frac{e\bar{\psi}}{kT} \right) \quad . \quad . \quad . \quad (380)$$

¹ Gouy, *Compt. rend.*, **149** (1909), 645; *Ann. Phys.*, (9), **7** (1917), 119.

D. L. Chapman, *Phil. Mag.*, **25** (vi) (1913), 470.

and the total effective charge—i.e., the electric density—is from (379) and (380)

$$\rho = en_0 \left[\exp. \left(-\frac{e\bar{\psi}}{kT} \right) + \exp. \left(+\frac{e\bar{\psi}}{kT} \right) \right]. \quad (381)$$

Applying Poisson's equation and choosing the plane of the electrode as $x = 0$, so that over any plane parallel with this, $\bar{\psi}$ is constant, (381) becomes

$$\nabla^2 \bar{\psi} = \frac{\partial^2 \bar{\psi}}{\partial x^2} = -\frac{4\pi en_0}{\rho} \left[\exp. \left(-\frac{e\bar{\psi}}{kT} \right) + \exp. \left(+\frac{e\bar{\psi}}{kT} \right) \right] \quad (382)$$

which by integration gives, first :

$$\frac{\partial \bar{\psi}}{\partial x} = \pm \sqrt{\frac{8\pi n_0 kT}{D}} \left[\exp. \left(+\frac{e\bar{\psi}}{2kT} \right) - \exp. \left(-\frac{e\bar{\psi}}{2kT} \right) \right] \quad (383)$$

and on further integration :

$$\frac{kT}{e} \ln \frac{\exp. \left(\frac{e\bar{\psi}}{4kT} \right) - \exp. \left(-\frac{e\bar{\psi}}{4kT} \right)}{\exp. \left(\frac{e\bar{\psi}}{4kT} \right) + \exp. \left(-\frac{e\bar{\psi}}{4kT} \right)} = x \sqrt{\frac{8\pi n_0 kT}{D}} + C' \quad (384)$$

$$\begin{aligned} \text{or } \ln \frac{\exp. \left(\frac{e\bar{\psi}}{4kT} \right) - \exp. \left(-\frac{e\bar{\psi}}{4kT} \right)}{\exp. \left(\frac{e\bar{\psi}}{4kT} \right) + \exp. \left(-\frac{e\bar{\psi}}{4kT} \right)} &= x \sqrt{\frac{8\pi n_0 e^2}{DkT}} \quad (385) \\ &= \kappa x + C' \end{aligned}$$

where κ , having the inverse dimensions of a length, has been substituted as in (261) for the quantity under the square-root sign. An expression is thus obtained for the potential at any point distant x from the electrode inside the double layer. The boundary conditions do not allow the constant C' to be evaluated, but as the Boltzmann equation has been applied, the analysis can only be valid for very dilute solutions—that is, for those in which $e\bar{\psi}/4kT$ is very small. Then (385) becomes :

$$\ln \frac{2e\bar{\psi}}{4kT} / 2 = \ln \frac{e\bar{\psi}}{4kT} \simeq \kappa x + c' \quad (386)$$

Between the potential $\bar{\psi}$ at a distance x from the electrode

in the double layer, and the potential $\bar{\psi}_0$ at the electrode, (386) will become :

$$\ln \frac{e\bar{\psi}}{4kT} - \ln \frac{e\bar{\psi}_0}{4kT} = \kappa x \quad . \quad . \quad . \quad (387)$$

$$\text{i.e.} \quad \frac{\bar{\psi}}{\bar{\psi}_0} = e^{\kappa x} \quad . \quad . \quad . \quad . \quad (388)$$

Calculations show that for aqueous solutions of monovalent ions in normal solutions,

$$\frac{1}{\kappa} = \sqrt{\frac{DkT}{8\pi n_0 e^2}}$$

approximates to 10^{-8} cm. Thus if x is of the order of an ionic radius (10^{-8} cm.)

$$e^{\kappa x} \simeq e$$

and from (388) the potential will have fallen at this distance from the electrode surface to about one-third of its value at the electrode. At double the distance—i.e., about 2×10^{-8} cm.—the potential will have only about $\frac{2}{13} \left(\approx \frac{1}{e^2} \right)$ of its initial value.

An application of the Boltzmann equation to the Gouy diffuse electric double layer at a metal solution interface shows therefore that almost the whole of the charge would reside within a distance of one or two molecular thicknesses of the electrode. The analysis assumes very idealised conditions to hold within the solution, and takes no account of the thermal agitation or the adsorption forces which have led to Stern's theory of the diffuse double layer. It is, however, fairly certain that within the inner double layer, where these conditions are approximately fulfilled, the potential does fall off very approximately exponentially over a short distance away from the electrode before perturbing factors become important.

Theory of the Diffuse Double Layer (Stern).

The equivalent thickness of this type of diffuse double layer just discussed is, however, much less than the observed values, and, further, Gouy's theory will not account for the observed phenomena of electrokinetic potentials, such as

the streaming potentials set up when a liquid electrolyte is flowed through a fine capillary. These results can, however, be explained satisfactorily if it be supposed that, even when the thermal agitation considered by Gouy is allowed for, there are also forces of adsorption acting on ions on the liquid side of the interface, and that there is, in immediate proximity to the interface, a parallel layer of charges of very small thickness.¹ The distribution of charges within the double layer falls therefore into two regions: one next to and parallel with the interface, having a small thickness of the order of the mean ionic radius and within which the charges are relatively fixed, the other the diffuse part of the double layer which stretches out into the solution, in which the charges are controlled by forces due to thermal agitation and adsorption. Here the ions are free to move in and out of the double layer subject to an equilibrium being maintained between the ions in solution and in the outer double layer. It is within this latter region that the charges are associated with the Freundlich ζ potential (for this is largely influenced by the presence of foreign electrolytes in the body of the liquid²) and the electrokinetic phenomena of electrolytes in contact with an interface are therefore due to the effects of this mobile or diffuse portion of the double layer.

The charges distributed over the whole double layer will be associated with the interface potential E (see Fig. 67), and it is therefore quite possible for the Freundlich potential to be negative while the interface potential is positive. There is, in fact, no relation between the ζ potential for a given interface as measured for example by the streaming E.M.F., and the Nernst interface potential for the same boundary.³ Attempts to measure the absolute zero of potential, therefore, by reducing the electrophoretic mobility of a metal colloid ion to zero, where $\zeta = 0$, must fail, since here there is no reason to suppose that the interface potential E is

¹ O. Stern, *Z. Electrochem.*, **30** (1924), 508.

² See, for example, the influence of electrolytes on the nature and sign of the double layer, studied by Perrin (*J. Chim. Phys.*, **II** (1904), 601) by electric endosmose experiments.

³ Freundlich and Rona, *Sitz. Preuss. Akad. Wiss.*, **20** (1920), 397.

also zero. The latter is determined solely by the concentration of the ions in the solution.

If we now suppose that the excess of positive charge on the electrode side of the double layer over the negative charge is ξ_0 , and that, at the boundary I which terminates the rigid part of the double layer, ξ_1 represents the net charge of the inner layer of the boundary, we may write :

$$\xi_0 = \xi_1 + \xi_2 \quad . \quad . \quad . \quad (389)$$

Here ξ_2 is used to denote the net charge in the adsorbed

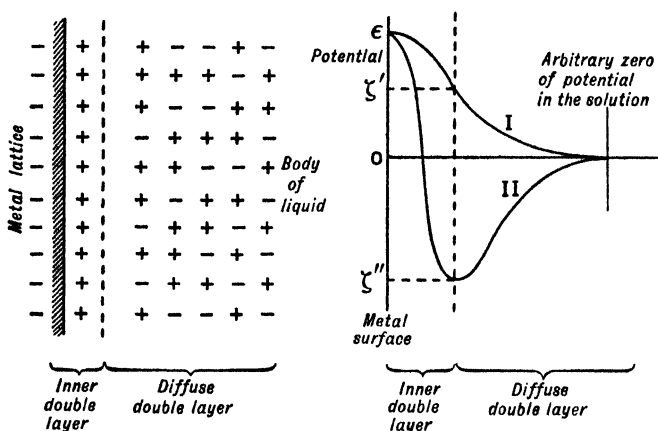


FIG. 67.—THE ELECTRIC DOUBLE LAYER AT A METAL SOLUTION INTERFACE (diagrammatic).

(diffuse) part of the layer from the boundary I out into the solution. The Helmholtz theory will now correspond with the condition that $\xi_2 = 0$, while the Chapman-Gouy theory corresponds to $\xi_1 = 0$. Putting $\bar{\psi}_1$ equal to the potential at the boundary I and $\bar{\psi}_0$ that at the electrode surface (boundary O), the total charge per unit square cm. at the electrode, due to the double layer is :

$$\xi_0 = K_0(\psi_0 - \psi_1) \quad . \quad . \quad . \quad (390)$$

or from (389) and the electrostatic expression for the capacity of a parallel plate condenser :

$$\xi_0 = \xi_1 + \xi_2 = \frac{\bar{D}}{4\pi\delta}(\psi_0 - \psi_1) \quad . \quad . \quad (391)$$

In these equations K_0 is the capacity of the "Helmholtz double layer condenser," δ its thickness, and $\bar{D}$ the mean dielectric constant of the solution over the range δ . A detailed analysis¹ shows that

$$\xi_0 = FZ \left[\frac{1}{2 + \frac{1}{c} \exp. \left(\frac{\phi - F\bar{\psi}_1}{RT} \right)} - \frac{1}{2 + \frac{1}{c} \exp. \left(\frac{\phi_- + F\bar{\psi}_1}{RT} \right)} \right] + \sqrt{\frac{DR\bar{T}}{2\pi \cdot 18}} \exp. \left(\frac{F\bar{\psi}_1}{2RT} - \frac{F\bar{\psi}_1}{2RT} \right) \quad (392)$$

where Z = number of gram-moles on 1 sq. cm. area of water approximating to 1.7×10^{-9} , ϕ_+ and ϕ_- are the specific adsorption potentials of ions which are defined as the free energies of formation of an "adsorbed layer" from one gram-mole of positive or negative ions with conditions defined by $\xi = 0$, and c = concentration of the solution as a molar fraction.

Philpot² has shown that according to equation (392) a plot of the charge density in the diffuse part of the double layer against the potential of the electrode surface will show two nearly linear sections with different slopes joined by a non-linear section. From measurements made on the surface of mercury with a dropping mercury cathode in solutions of hydrogen and sodium chloride, Philpot shows that the results conform very well with the predictions of Stern's theory. The Nernst-Helmholtz theory, on the other hand, would predict a completely linear curve for the variation, while according to the Chapman-Gouy theory of a diffuse double layer, the variation would be totally non-linear. These conclusions are confirmed by measurements of the capacity of the double layer made by passing direct and oscillatory discharges across the interface connected in series with an inductance.³ The results obtained from the oscillatory discharge are then always the very much smaller of the two sets of readings, and this difference may be very well attributed to the fact that, in the direct method, the

¹ O. Stern, *loc. cit.*

² J. St. L. Philpot, *Phil. Mag.*, **13** (vii) (1932), 775.

³ A. G. Clark, *Proc. Roy. Soc. Canada*, **18** (iii) (1924), 275; compare Frumkin and Proskauer, *Trans. Faraday Soc.*, **31** (1935), 112.

capacity determined is that of the whole double layer, while in the oscillatory discharge the mobile or diffuse part is reversed at each successive half wave of the discharge, so that the effective capacity measured under these conditions approximates to that of only the inner double layer.

The theory of the electric double layer receives additional confirmation from its ability to explain successfully many of the properties of solid-liquid colloid systems by assuming such a distribution of the charges to exist at the interfaces. Thus the permanency of the charge on a colloid ion, the protective action of certain colloids on metal sols and on emulsions, and the coagulation of these systems by the addition of a sufficient quantity of ions of the opposite sign to that of the colloid particles and the dependence of the extent of coagulation on the valency of the added ion (Hardy-Schultz law), have all received an adequate interpretation in terms of the modified double layer theory.¹

It might be thought that since the distance between successive atoms in the surface layers of a metal are large compared with the size of an electron, the latter might be able to penetrate the comparatively large spaces which the diffuse double layer will offer. A simple electrostatic consideration shows at once, however, that this cannot be the case.² For, every charged particle on either side of the double layer is surrounded by equipotential surfaces, and for successive charged particles many of these will join together forming, along both sides of the interface, a continuous set of equipotential surfaces. An electron or other charged particle entering the double layer will therefore require the expenditure of the same energy no matter at what point it penetrates the double layer; for, in penetrating the closed equipotential surfaces round a charged particle in the double layer, it has to cross these twice, and in consequence no work is done in the process. The number of extended equipotential surfaces, on the other hand, is the same all along the interface. It would there-

¹ See for example Rideal, "Surface Chemistry," Cambridge, 1930, pp. 382 *et seq.*

² R. W. Gurney, "Ions in Solution," Cambridge, 1937, pp. 39 *et seq.*

fore be perfectly permissible to treat the double layer simply as a condenser in the manner followed by Helmholtz. On the other hand, from our knowledge of the diffuse nature of the double layer it would be difficult in this simplified electrostatic picture to fix either the charge on the plates or the distance between them in our imaginary condenser.

The Seat of the E.M.F.

Until recently it was generally tacitly assumed that the seat of the E.M.F. of a galvanic cell was at the metal solution interfaces, since thermodynamic considerations of the energy changes taking place in the cell gave a satisfactory explanation of the observed phenomena in almost every case. In consequence of this agreement between theory and experiment, the Nernst solution pressure theory, which sought to give a mechanism for the operation of the galvanic cell, was allowed to pass almost unchallenged. There have, however, been criticisms raised in view of the difficulties encountered in understanding the exact significance of the solution pressure. Calculations of the solution pressure of a metal are obviously possible if the electrode potential is known when it is in contact with a solution of its own ions having a calculable osmotic pressure. Le Blanc¹ worked out some of these solution pressures for various metals, and showed that they ranged from comparatively high values, as for zinc, to so small a value as 1.5×10^{-36} for palladium. The difficulty which was encountered here had been expressed by Leffeldt² in the following terms: "If it is true that the fluids consist of molecules with a diameter of the order of 10^{-8} cm., then the production of a pressure so low (as for palladium) is impossible; for the pressure is a statistical effect due to the impact of numerous molecules, and in order to give such a pressure the solution would have to contain only one or two molecules of palladium in a space the size of the earth." Leffeldt also calculated the quantities of metal which would have to pass into ions per sq. cm. of immersed surface when the

¹ Le Blanc, "Electrochemie," Leipzig (1925).

² R. A. Leffeldt, *Phil. Mag.*, **48** (v) (1899), 430.

electrode metal has a large solution pressure of many hundreds of atmospheres. It appeared (for example) that in order to produce the solution pressure attributed to zinc, 1.27 gms. of metal per sq. cm. of surface would have to pass into the ionic form (actually a recalculation gives the figure as 3×10^{-9} gm). He therefore concluded that the "theory of concentration cells has been too hastily applied and without sufficient experimental confirmation." The first of these criticisms was met at the time¹ on the ground that it failed to realise the true significance of the Nernst concept of a solution pressure, since this was only intended as a measure of the *tendency* for ions to leave the metallic lattice and to pass into the solution. Nevertheless the postulated value of the solution pressure had been used by Nernst in deducing an expression for the electrode potential on the same principle as that used with the osmotic pressure of ions in the solution. Smits pointed out, moreover, that as Nernst assumed a metal to consist of ions and electrons, there should be a heterogeneous equilibrium between electrons in the metal and electrons in the electrolyte which would have to be accounted for in the deduction of the potential difference.²

A further and most important difficulty in the Nernst theory has arisen from the study of metal-metal contact E.M.F.'s.³ Einstein⁴ and Richardson and Compton⁵ have dispelled the notion that these Volta potentials are due to such external causes as atmospheric action, and have established that, apart from the small Peltier effects at the junction of two metals, the contact potential difference is given by :

$$V = e(\phi_2 - \phi_1) = eh(\nu_1 - \nu_2) \quad . \quad . \quad (393)$$

where ϕ_1 and ϕ_2 are the thermionic work functions and ν_1 and ν_2 the threshold frequencies of the two metals. Calculations of the Volta potentials show that these are of

¹ F. Kruger, *Z. physikal. Chem.*, **35** (1900), 18.

² Smits, "Theory of Allotropy," London (1922), p. 115.

³ E. K. Rideal, *Trans. Faraday Soc.*, **19** (1924), 667.

Heyrovsky, *J. Physical. Chem.*, **29** (1906), 344.

⁴ Einstein, *Ann. Physik*, **20** (1906), 203.

⁵ Richardson and Compton, *Phil. Mag.*, **24** (vi) (1912), 592.

the same order as the E.M.F.'s of the cells having the same two metals as electrodes. Moreover the electrochemical order of the metals is almost identical with that for the contact potentials measured between each metal and some standard metal, and it therefore appears necessary to assume that the measured E.M.F. of a galvanic cell consists largely of the contact potential in the external circuit. Further evidence in confirmation of this view is given by the fact that the E.M.F. of a galvanic cell is almost independent of the solvent which is used in making up the cell solution,¹ for if the measured E.M.F. has its origin almost exclusively in the external circuit it will be affected by a change in the nature of the cell solution only in so far as the overall E.M.F. may include small potentials developed at the interfaces. It is therefore necessary to distinguish carefully in the measured E.M.F. between the Volta potential and the interface potentials which will be set up at any metal-liquid surface, all of which are included in the "electrode potential."

The Statistical Theory of the Galvanic Cell.

We have just seen that the Volta potential in the external circuit of a galvanic cell must not be ignored in attempting to account for the measured E.M.F. of the cell. There remains, however, the unquestionable fact that the E.M.F. of a galvanic cell is related exactly to the energy change proceeding in the cell, and these two lines of evidence must, in some way, be correlated. Butler first showed that the two views were not mutually exclusive² by developing statistically the theory of metals which regards these as completely ionised.³ Sommerfeld⁴ has extended this theory by supposing that all the valency electrons in the lattice are quasi-free, behaving as a degenerate gas with abnormally high mean free paths, but that all the atoms participate

¹ Buckley and Hartley, *Phil. Mag.*, **8** (vii) (1929), 320.

McAulay and Spooner, *Proc. Roy. Soc.*, **A**, **138** (1932).

² J. A. V. Butler, *Trans. Faraday Soc.*, **19** (1924), 729; *Phil. Mag.*, **48** (vi) (1924), 927.

³ J. J. Thomson, *Phil. Mag.*, **43** (vi) (1926), 721.

⁴ Sommerfeld, *Ber.*, **61** (1928), 1171.

equally in supplying these electrons until the metal is disturbed at its surface. On this view the surface layer of a metal will be composed exclusively of ions, and when the metal is immersed in a solution of its own ions, there will be an equilibrium between the ions in the solution and in the metal, in which the number deposited from the solution is equal to the number in the metal which can overcome the highly localised attractive force. The balance point will be somewhere in the solution at a small distance from the electrode, since this attractive force falls off very rapidly

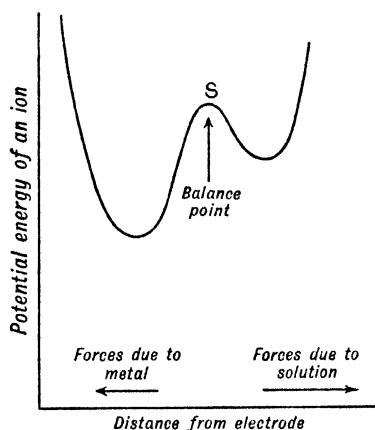


FIG. 68.—ENERGY DIAGRAM NEAR A METAL SOLUTION INTERFACE.

with distance. The position of the balance point will of course depend on the magnitude of the interface potential E . If the surface of the metal is positively charged with respect to the solution, the total work per gram-ion done by a positive charged ion passing out of the surface layer of the lattice into the solution is zEF . At equilibrium, the number of ions per unit time, θ_1 reaching the point S from the metal is equal to the number, θ_2 arriving there

from the body of the solution, so that, knowing the work done in each case, the proportion of ions reaching the balance point from each direction may be calculated from Boltzmann's theorem. The work which an ion must do to reach the balance point, from whichever direction it approaches, will consist of two parts: firstly the work W required to overcome the combined attractive forces of the metal surface and the liquid to reach S (Fig. 68), and secondly the work, $-zEF$ required to overcome the electrostatic attraction of the surface on the solution. The total number of ions reaching the balance point in unit time is therefore in either case:

$$\theta = N\sqrt{TA} \exp\left(-\frac{W - zEF}{RT}\right) \quad . \quad (394)$$

N being the number N_1 of ions per square cm. of surface when the ions come from the metal or the number N_2 of ions per unit volume exerting the attractive force on the solution side of the balance point, and A the statistical constant. Thus at equilibrium :

$$\theta_1 = \theta_2 \quad . \quad . \quad . \quad . \quad . \quad (395)$$

i.e., from (394) :

$$\begin{aligned} N_1 \sqrt{T} A_1 \exp. \left(- \frac{W_1 - zE_1 F}{RT} \right) \\ = N_2 \sqrt{T} A_2 \exp. \left(- \frac{W_2 - zE_2 F}{RT} \right) \quad . \quad (396) \end{aligned}$$

$$\text{or} \quad \frac{W_2 - W_1}{RT} + \frac{zF(E_1 + E_2)}{RT} = \ln \frac{N_2 A_2}{N_1 A_1} \quad . \quad (397)$$

The heat absorbed in the passage of a gram-ion of a metal into the solution is equal to the total difference between the work terms $W_2 - W_1 = U$, and since the total potential difference between the metal and the solution is the sum of the potential differences from either side to the balance point

$$E = E_1 + E_2 = E_0 + \frac{RT}{zF} \ln a \quad . \quad . \quad (398)$$

$$\text{i.e.,} \quad E = \frac{U}{zF} + \frac{RT}{zF} \ln \frac{N_2 A_2}{N_1 A_1} \quad . \quad . \quad . \quad (399)$$

Expressing now the concentration of ions in the solution N_2 , in terms of grams per 1000 c.c.s

$$N_2 = \frac{NC}{1000}$$

(N being the Avogadro number) and (399) becomes :

$$E = \frac{U}{zF} + \frac{RT}{zF} \ln \frac{N^* A_2}{1000 N_1 A_1} + \frac{RT}{zF} \ln c \quad . \quad (400)$$

A comparison of this with the Nernst expression (373) shows that if p be the solution pressure,

$$\ln p = \frac{U}{RT} + \frac{RT}{zF} \ln \frac{N A_2}{1000 A_1 N_1} \quad . \quad . \quad (401)$$

and the solution pressure includes not only a concentration term, but also a term U/RT depending on the difference of

energy of the ions in the two phases, a factor which may be very large. The large values calculated by Le Blanc and Lehfeldt for the solution pressure are not therefore impossible on physical grounds.

For the whole galvanic cell in which, say, the reaction



takes place, there are three distinct processes, each involving a separate energy change :

(a) at the metal electrode $M \longrightarrow M_{aq.}^+ + \epsilon + U_1$;

(b) at the metal-metal junction there is, on Richardson and Compton's theory, a transfer of electrons involving, per gram-electron, an energy change $U_3 = F(\phi_1 - \phi_2)$;

(c) at the hydrogen electrode $H_{aq.}^+ + \epsilon = \frac{1}{2}H_2 + U_2$

and the entire heat of reaction is therefore given by

$$Q = U = U_1 + U_2 + U_3 = (U_1 + U_2) + F(\phi_1 - \phi_2) \quad (402)$$

Of the unknown quantities in this equation, U_1 and U_2 may be determined independently by carrying out a Born cycle on the process. If now $[M]$ represent the concentration of metal ions in the solution, equation (399) gives for the corresponding interface potential :

$$e_1 = \frac{U_1}{zF} + \frac{RT}{zF} \ln K_1 + \frac{RT}{zF} \ln [M] \quad . \quad (403)$$

For the hydrogen electrode, assuming that the relation for the interface potential is of the same form as for a substance in which electrons are exchanged from the substance in one state of oxidation to another, Butler calculates ¹

$$e_2 = -\frac{U_2}{zF} + \frac{RT}{zF} \ln K_2 + \frac{RT}{zF} \ln \frac{[H^+]}{[H_2]^{\frac{1}{2}}} \quad . \quad (404)$$

and at the metal-metal junction a statistical analysis of the rate of gain and loss of electrons ² shows that :

$$e_3 = -\frac{F(\phi_1 - \phi_2)}{zF} + \frac{RT}{zF} \ln K_3 \quad ; \quad . \quad (405)$$

¹ Butler, *Trans. Faraday Soc.*, **19** (1924), 729, 734.

² *Idem*, *Phil. Mag.*, **48** (vi) (1924), 746.

i.e., for the entire cell :

$$E = e_1 - e_2 - e_3 = \frac{U}{zF} + \frac{RT}{zF} \ln [M] - \frac{RT}{zF} \ln \frac{[H^+]}{[H_2]^{\frac{1}{2}}} + \frac{RT}{zF} \ln K \quad . \quad . \quad (406)$$

By differentiation (406) gives the Gibbs-Helmholtz equation :

$$E - \frac{U}{zF} = T \frac{\partial E}{\partial T} \quad . \quad . \quad . \quad (407)$$

It follows therefore that, although the Nernst view that the only source of the E.M.F. is at the metal-solution interface is no longer tenable, the view that the seat of the E.M.F. is chiefly at the metal-metal junction, with small contributions from the metal-solutions interfaces, is complementary with the theory that the energy changes taking place in the cell are responsible for the E.M.F.

Quantum Mechanical Considerations.

The functions of the different interfaces in determining the E.M.F. have been made clearer, and Butler's statistical analysis has at the same time been generalised, by quantum mechanical considerations of the state of affairs at each electrode interface.¹ An ion surrounded by neutral metal atoms in a lattice has a charge not of $\pm e$, but of some fraction $\pm \eta e$ of this, this charge being received from the wave-functions of all the surrounding atoms. In removing an ion from the lattice, since the ion then ceases to participate, work is done in separating the charges, giving rise to a potential curve of the type *MN* (Fig. 69). If the ion now approaches a water molecule, the potential falls due to hydration, the magnitude of the fall depending on the magnitude of the hydration energy. The entire potential energy curve of an ion leaving the lattice and approaching a water molecule in

¹ R. W. Gurney, *Proc. Roy. Soc., A*, **136** (1932), 378; "Elementary Quantum Mechanics," Cambridge (1934), pp. 80, 81.

R. W. Fowler, *ibid.*, **A**, **136** (1932), 391, gives a generalised statistical derivation of the Gibbs-Helmholtz equation following Gurney's theory, by first calculating the value of the interface potential in terms of the concentration of the metal ions in the solution, and hence a value for the E.M.F. of the whole cell.

the solution has therefore either of the forms I or II in the figure. In the former case therefore, to be called a *d* situation, at the lowest temperatures where only ground levels

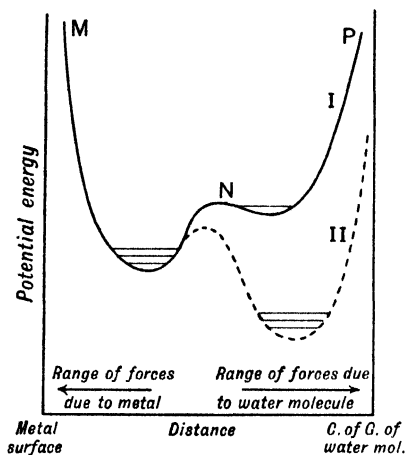
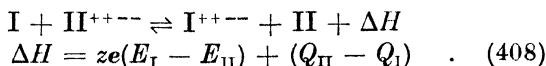


FIG. 69.—ENERGY DIAGRAM NEAR A METAL-SOLUTION INTERFACE (Gurney).

are occupied, transition takes place from solution to metal, but in the type of potential energy curve represented by II, termed the *s* situation, the transitions are in the reverse direction. Denoting by Q_I the amount of energy liberated by the change in levels due to the transition from metal to solution of a metal ion I, and by E_I the interface potential, an amount of heat $(Q_I - zE_I e)$ is liberated per ion dissolved. So for

a metal ion II passing from the solution into the lattice, heat $(Q_{II} - zE_{II} e)$ is evolved¹ and for the whole exchange reaction



If now the metals are actually in contact with each other, they are at a potential difference $z[E_I - E_{II}]$, and since electronic transitions are much more rapid than ionic ones, this quantity is approximately equal to the Volta potential V ; thus from (408) we have :

$$\Delta H = Ve - (Q_{II} - Q_I) \quad (409)$$

As, however, $Q_{II} - Q_I$ is normally small compared with the first term, this equation becomes to a first approximation :

$$\Delta H = Ve \quad (410)$$

a relation which indicates the very close connection between the heat of chemical reaction and the Volta potential, which any theory of the galvanic cell must explain.

¹ This assumes that the two metals give ions with the same valency z .

At the metal junction, the electrons in the two metals occupy different levels until contact is made, when electrons pass across the boundary, which acts as a potential barrier, and fill unoccupied levels in the second metal. This continues until the levels in each metal are at the same height, when the potential difference set up is just sufficient to stop further transitions. This small displacement of levels which occurs (a lowering of electron levels becoming a rise of positive ion levels) *when the external circuit is closed* is just sufficient to raise the ion levels in the metals (see Fig. 65 I) until the *s* situation is reached, and solution of the base metal and deposition of the noble metal can take place continuously, giving rise to the observed E.M.F.

The function of the metal-metal contact in the galvanic cell is therefore of the utmost importance, since the cell reaction can only proceed as a result of the modification of the electron levels which takes place here and gives rise to the Volta potential. The chemical and physical interpretations of the E.M.F.'s observed in galvanic cells, far from being mutually exclusive, are both processes taking place in a chain of events when the external circuit of the galvanic cell is closed—*i.e.*, when the metal-metal contact potential is established. The thermodynamic interpretation takes account only of the chemical events in the chain, and the kinetic considerations of the various interface potentials are confined to the physical events. Thus, while both of these give results agreeing with experiment, they each represent only a part of the whole sequence. The true sequence of changes in a galvanic cell is, however, completely disclosed by the quantum mechanical considerations of the events taking place at each particular stage.

CHAPTER IX

REVERSIBLE CELLS

Standard for Electrode Potential Measurements.

THE normal electrode potential E_0 of an electrode is given by the logarithmic expression (375) :

$$E = E^0 - \frac{RT}{zF} \ln a$$

and unless therefore there is some method of determining E_0 absolutely, it will be possible to measure E only in terms of its differences against some arbitrary zero or against the potential of some other part of the system. Many attempts have been made to determine the absolute values of the standard electrode potentials using capillary electric methods,¹ but none of these has been successful. For they assume that at the maximum of the electrocapillary curve (*i.e.*, the curve which shows the variations of the potential difference between a metal surface and a solution of its ions, with changes in the surface tension) the charge on the metal surface becomes zero because the interfacial potential is zero at this point. But it has been shown that the ζ potential, which is the potential that does become zero at this point, is by no means the same thing as the interfacial potential, and it does not follow that the latter is also zero when $\zeta = 0$.² It will therefore not be possible to determine the interfacial potential on an absolute scale in this manner, and failing such an absolute standard, electrode potentials must be defined with reference to some arbitrarily chosen standard of potential. This agreed universal standard of potential for which E^0 in equation (375) is zero is, at all temperatures, the potential of a hydrogen electrode defined

¹ *E.g.*, J. Billitzer, *Trans. Amer. Electrochem. Soc.* (1930); *Z. Electrochem.*, **37** (1931), 736.

² A. Frumkin, "Colloid Symposium Annual" (vii) (1930), p. 103.

as formed by the passage of hydrogen gas at one normal atmosphere pressure over catalytically active platinum in contact with a solution of hydrogen ions at unit activity. *Only to a first approximation* will this be the same as the potential of an electrode defined with a solution containing 1 gram-ion of hydrogen ions per litre which Abegg uses in defining the standard hydrogen electrode,¹ since different acids give very different values for the activities of their hydrogen ions when the concentrations calculated from their conductivities are unity.²

Substandards for Electrode Potential Measurements.

The hydrogen standard is not altogether the most convenient *practical* standard for purposes of measurement, owing to the sensitiveness of the platinum catalyst to many substances, but any reversible non-polarisable electrode with an accurately reproducible E.M.F. may be used as a sub-standard. The most convenient of these sub-standards is the calomel electrode (Fig. 70) in which the electrolyte is a standard solution of potassium chloride (N/10 or N) saturated with calomel by the presence of an excess of this. The calomel must be kept free from mercuric chloride by the addition of mercury to it. This mixture is then placed over a mercury electrode at the bottom of the cell vessel. We may therefore represent the electrode reactions as :

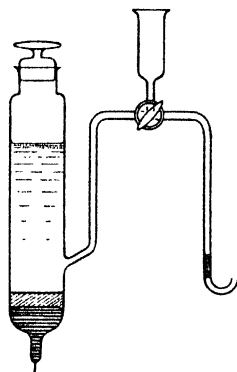
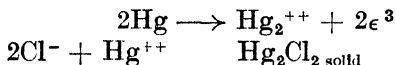


FIG. 70.—THE CALOMEL ELECTRODE.

¹ Abegg, Auerbach, and Luther, "Messungen Electromotische Kräfte galvanische Ketten" (1911).

² Lewis and Randall, "Thermodynamics" (1923), p. 404.

³ The mercurous ion has been shown to be divalent by Ogg (*Z. physikal. Chem.*, 27 (1898), 285) from measurements of the E.M.F. of the cell



This conclusion has been confirmed by the freezing-point depressions of dilute nitric acid solutions due to the presence of mercurous nitrate.

The electrode behaves reversibly, since there is always a large excess of chlorine ions present from the potassium chloride, and the passage of a small current through the electrode causes no appreciable alteration in their concentration. A simple consideration will show that the calomel electrode is strictly equivalent to a reversible chlorine electrode. For from (375) the potential of the electrode will be :

$$E = E^0 - \frac{RT}{2F} \ln (\text{Hg}_2^{++}) \quad . \quad . \quad (411)$$

where (Hg_2^{++}) denotes the mean activity of mercurous ions. Using now van 't Hoff's solubility product expression : ¹

$$(\text{Hg}_2^{++})(\text{Cl}^-)^2 = L \quad . \quad . \quad . \quad (412)$$

$$\text{i.e.,} \quad (\text{Hg}_2^{++}) = \frac{L}{(\text{Cl}^-)^2} \quad . \quad . \quad . \quad (413)$$

Substituting therefore from (413) in (411), we have :

$$E = E^0 - \frac{RT}{2F} \ln \frac{L}{(\text{Cl}^-)^2} = E^{01} + \frac{RT}{F} \ln (\text{Cl}^-) \quad (414)$$

Equation (414) is now of the type we should expect for a reversible chlorine electrode, so that the calomel electrode is therefore equivalent to this. Against the standard hydrogen electrode the decinormal calomel electrode has a potential at 25° C. of + 0.3351 volt,² whilst the normal calomel electrode with an N/10 potassium chloride solution as a liquid bridge ³

$$\text{Hg} \left| \begin{array}{c} \text{Hg}_2\text{Cl}_2 \text{ in a solution} \\ \text{of KCl containing one} \\ \text{mole per litre of solution} \end{array} \right| \frac{\text{N}}{10} \text{ KCl (liquid bridge)}$$

has a potential, against standard⁴ hydrogen, of + 0.2822 volt at 25° C.⁴ If, now, any electrode is measured against

¹ van 't Hoff, *Z. physikal. Chem.*, **3** (1889), 484. Since almost all measurements of the solubility product are made from E.M.F. measurements the ion functions are here represented as activities.

² Lewis, Brighton, and Sebastian, *J. Amer. Chem. Soc.* (1917), 2245.

Lewis and Randall, "Thermodynamics," p. 405.

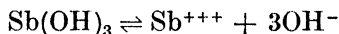
³ The potential of the normal calomel electrode is always expressed to include the liquid junction effect (see pp. 276-280).

⁴ H. S. Harned, *J. Amer. Chem. Soc.*, **38** (1916), 1986.

the decinormal calomel electrode and its potential is found to be E against this standard, its electrode potential will therefore be given by :

$$E^0 = E + 0.3351 \quad . \quad . \quad . \quad (415)$$

The antimony electrode has been widely used as a convenient substandard. Its E.M.F. depends on the dissociative equilibrium :



For this reaction, since the solubility product is

$$L = (\text{Sb}^{+++})(\text{OH}^-)^3 \quad . \quad . \quad . \quad (416)$$

the antimony ion activity (Sb^{+++}) will be :

$$(\text{Sb}^{+++}) = \frac{L}{(\text{OH}^-)^3} = \frac{L}{K_w} (\text{H}^+)^3 = K'(\text{H}^+)^3 \quad (417)$$

where

$$K_w = (\text{OH}^-)(\text{H}^+) \quad . \quad . \quad . \quad (418)$$

is the ionic product for water. The electrode potential of antimony in contact with a solution of its own ions is given by equation (375) as :

$$E = E^0 - \frac{RT}{3F} \ln (\text{Sb}^{+++}) \quad . \quad . \quad (419)$$

or, substituting from (417) :

$$E = E^0 - \frac{RT}{3F} \ln K'(\text{H}^+)^3 = E^0' - \frac{RT}{F} \ln (\text{H}^+) \quad (420)$$

giving an expression which is exactly analogous to that for the potential of the hydrogen electrode. In a similar manner, the quinhydrone electrode (see p. 316), involving a typical redox system, can be shown to be equivalent to a hydrogen electrode, and it is often used as a substandard in place of the calomel electrode. For biochemical work a glass electrode is frequently used. The action of this depends on the differences of potential set up at the boundary of the acid or alkaline solution and a "solid solution" of water in a blown glass membrane.¹

¹ Haber and Klemensiewicz, *Z. physikal. Chem.*, **67** (1909), 355.
 MacInnes and Dole, *J. Amer. Chem. Soc.*, **52** (1930), 29.
 W. S. Hughes, *J. Chem. Soc.* (1928), 491.
 Mrs. P. T. Kerridge, *Biochem. J.*, **19** (1925), 611.

The Hydrogen Electrode.

Although any of the electrodes enumerated in the last section may be used for special purposes as substandards, their use is limited by the conditions of the problem. The quinhydrone electrode is limited in its application, for example, to solutions on the acid side of neutrality. It is therefore necessary that the hydrogen electrode itself should always be reproducible with the highest possible degree of accuracy. A simple immersion electrode of the Hildebrande type¹ (Fig. 71), although valuable for ordinary laboratory measurements where an accuracy of a few millivolts is

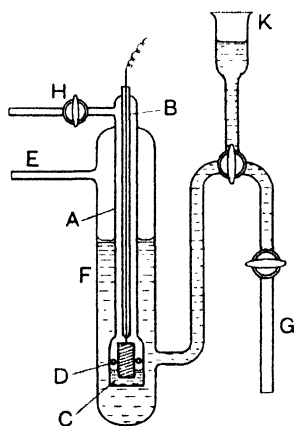


FIG. 71.—HILDEBRANDE'S HYDROGEN ELECTRODE.

sufficient, suffers from many faults which do not recommend it as the type of electrode to be chosen for a standard. Clark² has given a critical review of the difficulties encountered in the ordinary designs of hydrogen electrodes, and he has designed a very accurate and reproducible cell in which the equilibrium is attained with rapidity. It has been shown³ that the chief condition which should be fulfilled for the reproducibility of the hydrogen electrode, is to keep the solution shaken constantly so that the electrode is only exposed periodically to the gas. In this way the hydrogen is required to penetrate a thin film of liquid before being adsorbed on the platinum. A further condition for the accurate reproducibility of the potential of a cell containing a hydrogen half element, is the saturation with hydrogen of the whole of the solution used to connect the half-cell with the liquid bridge.⁴ Clark's cell (Fig. 72) incorporates these

¹ Hildebrande, *J. Amer. Chem. Soc.*, **35** (1913), 847.

Lewis, Brighton, and Sebastian, *ibid.*, **39** (1917), 2245.

² W. Mansfield Clark, *J. Biol. Chem.*, **23** (1915), 475.

W. M. Clark, "The Determination of Hydrogen Ions" (1928), pp. 290, 302.

³ J. A. Hasselbalch, *Biochem. Z.*, **30** (1911), 97; **49** (1913), 451.

⁴ S. F. Acree and C. N. Myers, *J. Amer. Chem. Soc.*, **35** (1913), 396.

improvements, the former by rocking the cell in such a manner that the liquid alternately surges over the platinum and then leaves it uncovered, the latter by designing the cell in such a way that the liquid junction proper is made as close as possible to the solution in immediate contact with the hydrogen. The cell is therefore arranged to have its greater length horizontal with the platinised platinum electrode¹ at one end immediately over the tube used for connecting the half-cell through the liquid junction. The whole apparatus is then rocked by an eccentric arrangement. After flooding with hydrogen, the vessel may be filled with the liquid to be measured from the container *B* through *A*, to a convenient depth sufficient to cover the

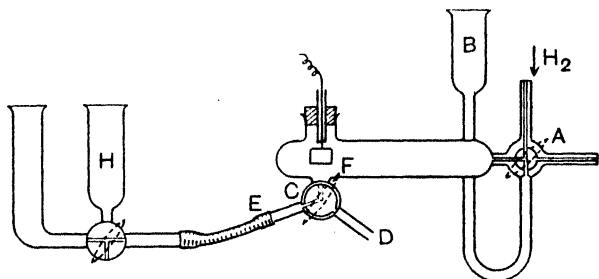


FIG. 72.—CLARK'S HYDROGEN ELECTRODE.

platinum completely when the *A* end is in its highest position, and yet to expose it in its lowest position. Hydrogen at atmospheric pressure is brought into contact with the solution through the side tube of *A*, and the difficult process of establishing the liquid junction is accomplished by flowing fresh saturated potassium chloride solution from *H* through *I* and out through *D*, and the flow stopped by closing *I*. By pinching the tube *E* and releasing it after turning *C* to connect with the cell liquid, the liquid junction is brought down into the wide tube below *C*. In this way a good conducting film of solution in the tap *I* connects the

¹ Platinisation is necessary to increase the superficial area of the platinum (Eggert, *Z. Electrochem.*, 21 (1915), 349). The process is carried out by making the platinum the cathode in a strong solution of ammonium chloroplatinate in strong hydrochloric acid. A platinum-wire anode is used during the electrolysis.

cell through the liquid in *C* with a calomel half-cell. Some little time (usually about five minutes) elapses after making these liquid junctions before the readings become constant, this being the time taken to attain equilibrium, but then they differ over successive intervals of time by not more than 0.0001 volt. Closer agreement than this would scarcely be profitable, for the uncertainties in the values of the liquid junction potentials usually amount, even under the best conditions, to more than this.

The Oxygen Electrode.

It is interesting at this point to consider the difficulties which are encountered in attempting to use an oxygen electrode, for although it is relatively easy to obtain consistent results for the potential of a hydrogen half-cell when this is connected with another reversible electrode, oxygen adsorbed on platinum does not behave at all in a thermodynamically reversible manner. The value 1.227 volts¹ at 0° and 760 mm. for the E.M.F. of a hydrogen-oxygen cell, calculated from thermal data, is, in fact, never reached in practice, and the irreversibility of the cell can only be ascribed to the oxygen electrode. T. P. Hoar² used a design similar to that illustrated in Fig. 73 for an oxygen electrode in his investigations of its mechanism. In order to ensure a uniform current density over the exposed surface of the platinum of the electrode, this is arranged horizontally as a disc of metal which has its upper surface coated with a resistant layer of wax, and the electrolyte solution is kept saturated with oxygen by passing a continuous stream of this gas over its surface. The theoretical reversible oxygen potential of 1.227 volts could never be approached unless the electrode was anodically polarised. From a study of the anodic polarisation curves on the same electrode used for a series of experiments, Hoar established that the irreversible process taking place at the oxygen electrode was the formation, within the cracks and pores of the oxide film which was always present

¹ Lewis and Randall, *J. Amer. Chem. Soc.*, **36** (1914), 1909.

² T. P. Hoar, *Proc. Roy. Soc., A*, **143** (1934), 628.

on the platinum,¹ of more oxide, due to the permeability of the film to the electrolyte. The resistance of the film therefore slowly rose, due to this auto-polarisation when the electrode was on open circuit, and in order to obtain the reversible potential, the electrode had to be anodically polarised to just such an extent as would prevent this

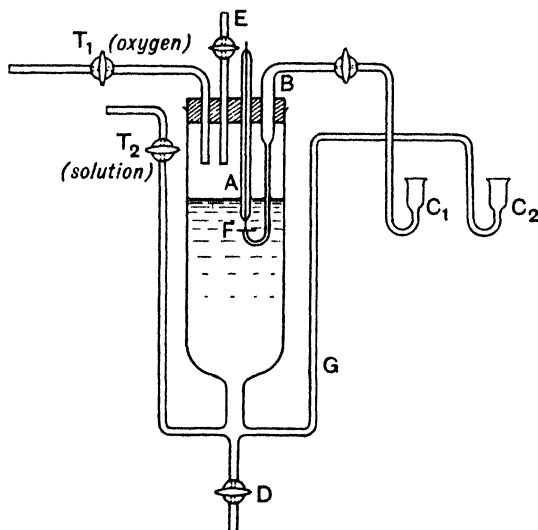


FIG. 73.—HOAR'S OXYGEN ELECTRODE.

irreversible process from taking place. The net electrode reaction



probably takes place therefore in stages, first by the absorption of oxygen on the oxide film already present on the platinum, followed by some process of activation and reaction of the oxygen with either charged or discharged cations, the rate of reaction being limited by that of the slowest stage. Due to the slowness of the above reaction at every known metal surface, compared with the rate at which electromotively active material is removed from the

¹ Mond, Ramsey, and Shields, *Proc. Roy. Soc.*, **58** (1895), 242; *ibid.*, **62** (1897), 50.

Lorenz, *Z. Electrochem.*, **14** (1908), 781; *ibid.*, **15** (1909), 157, 206, 293, 349, 661.

oxidised surface down the pores by the auto-polarisation process, it is impossible ever to attain the theoretical reversible oxygen potential in open circuit. At the same time, the extrapolated value 1.20 ± 0.03 at 15°C. obtained by Hoar from the cathodic and anodic polarizations curves, shows that the above reaction is the true electrode process, since this experimentally estimated value for the reversible potential agrees with Lewis's value 1.227 volts within the limits of experimental error. In spite of these difficulties, which render the oxygen electrode useless as a standard element, it is frequently used when, for purely chemical reasons, such as may arise with easily reducible solutions, the hydrogen or quinhydrone electrodes may not be used.¹ In these cases—as, for example, in the potentiometric titration of chromates, etc.—the oxygen electrode is first calibrated empirically against a series of solutions of known hydrogen-ion concentration, and the readings in these cases need never be to within more than a few millivolts in order to give a satisfactory end-point.

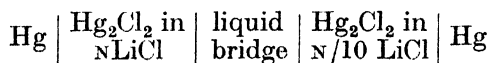
Liquid Junctions.

Now, we have assumed in the previous discussion of standard electrode potentials that it is possible to measure accurately the difference of potential between two electrodes when these are connected together. But before any measurements of standard electrode potentials may be made for the purpose of calculating the activity coefficients of solutions or the standard free energies of substances, it is necessary to connect together the electrode the potential of which is required, with a standard electrode, in such a manner that diffusion of the electrode solution is prevented, whilst the electrical circuit is completed. If diffusion of the solution from one electrode to the other were allowed to take place it would disturb the concentration of that solution, and might result in chemical reaction taking place. Moreover the connection should, if possible, be made so that the E.M.F. of the whole cell is actually the difference between the two electrode potentials, or so that it may

¹ Furman, *J. Amer. Chem. Soc.*, **44** (1922), 2685.

differ from this by a known or calculable amount. The only practicable method of joining together two such electrodes is through a liquid junction where direct diffusion between the electrode solutions is reduced to a minimum by intercepting a solution which does not react with either of them. In order to obtain reproducible results with such an arrangement, however, numerous technical difficulties have to be surmounted.

The simple liquid junction, established by bringing each electrode into contact with a common solution, is usually arranged so that the solutions meet in a fine sintered glass plug or in the annular space between the barrel and the key of an ungreased tap sealed into the side tube of each electrode vessel. In this way diffusion between the electrode solution and the inert solution of the liquid "bridge" is reduced to a minimum, whilst the electrical connection of the two solutions is established. The choice of the solution which is to form the inert bridge is of very great importance. Experience shows that the smallest deviations between the thermodynamically calculated values for the E.M.F. and the values observed experimentally when the electrodes are connected through a static liquid junction, are obtained when the bridge solution is a saturated solution of some uni-univalent electrolyte for which the anion and cation mobilities are, as nearly as possible, equal. Measurements on the cell



have been made using different bridge solutions with the results exhibited on p. 278 in Table VII.¹

Although it appears from these particular figures that a strong solution of ammonium nitrate is most efficient in reducing the liquid junction potential, it is certain that in general, far from eliminating it, it may even increase the uncertainty,² and potassium chloride in saturated solution is probably the most efficient liquid for a static liquid junction.

¹ See also Bjerrum, *Z. Electrochem.*, **17** (1911), 58.

Myers and Acree, *J. Amer. Chem. Soc.*, **35** (1913), 396.

² Lewis and Randall, "Thermodynamics" (1923), p. 399.

TABLE VII.

Values of Liquid Junction Potentials.

Bridge solution.	Anion transport number.	Cation transport number.	E.M.F. obs.	E.M.F. calculated thermodynamically.	Difference.
No bridge solution .	—	—	0.0361	0.0530	— 0.0169
N.NH ₄ NO ₃ solution .	0.487	0.513	0.0480	0.0530	— 0.0050
10N.NH ₄ NO ₃ .	—	—	0.0543	0.0530	+ 0.0013
Saturated KNO ₃ .	0.488	0.512	0.0510	0.0530	— 0.0020
Saturated KCl .	0.508	0.492	0.0515	0.0530	— 0.0015

For accurate determinations of the activity coefficients of solutions by the E.M.F. method it is absolutely necessary not only to be able to form liquid junctions which have the highest degree of reproducibility and stability, but also to be able to calculate their potentials as accurately as possible. The possibilities of dynamic junctions for liquid interfaces were first indicated by the fact that, using junctions of permeable parchment paper separating the two liquids, much greater reproducibility was obtained in dilute solutions if the solution immediately beneath the membrane was uniformly stirred, than if the junction remained static.¹ Again, when readings are taken immediately after the formation of a fresh junction, the liquid junction potential falls almost to zero, but rises, often by several millivolts, on standing, due to an "ageing" effect which can be traced to disturbing oscillations of the liquid in the membrane tube.² The reproducibility with the membrane method is, however, restricted to very dilute solutions, and in general the best results are obtained using a "flowing liquid junction." This is formed by flowing the lighter liquid from one electrode over the heavier liquid from the other in a T-tube where the mixed liquids can flow out together along the angle tube. A number of improvements have been made on the simple form of the flowing junction, which are designed to facilitate

¹ Lamb and Larson, *J. Amer. Chem. Soc.*, **42** (1920), 229.

² Lewis and Rupert, *ibid.*, **33** (1911), 299, showed that considerable changes in the liquid junction potential arose from "ageing," and they concluded that the most satisfactory values for a static junction were those observed as soon as possible after the junction had been established.

the formation of the junction (Fig. 74).¹ In order to prevent the formation of a "dead space" and to facilitate rapid flow, the tube *A* is constricted just opposite the T-tube, and the mixed liquids are led off at *C* at a constant level to avoid the slight pumping action which would disturb the boundary if the liquids were siphoned off. Liquids which differ appreciably in density would disturb the boundary if they were flowed in at the same rate, but by using cylindrical reservoirs, *D*₁, *D*₂, for these, with cross-sectional areas in inverse proportion to the densities, the rates of flow of the liquids adjust themselves until they are the same. The

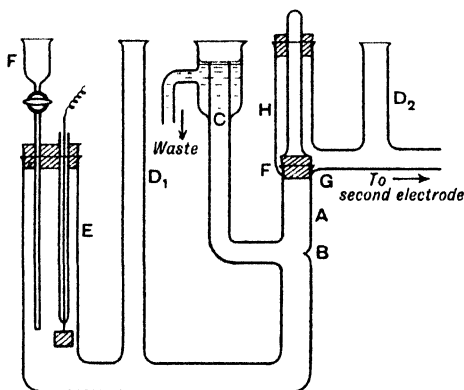


FIG. 74.—LAMB AND LARSON FLOWING JUNCTION.

solution forming the upper layer in the liquid junction may be cut off by the rubber plug *F*, and so, the two halves of the apparatus filled preparatory to establishing the junction, *without any appreciable diffusion taking place*.

Evidence for the nature of the flowing liquid junction has been obtained by using two neutral solutions to form the boundary. To one of these is added a trace of phenolphthalein, to the other a trace of caustic soda. Where the liquids meet, the solution becomes pink, and a surface of separation of almost microscopic thickness starts at the constriction *B*, and persists, with only a slight thickening, right up to the overflow at *C*. Lamb and Larson found in

¹ MacInnes and Yeh, *J. Amer. Chem. Soc.*, **43** (1921), 2563.
G. Scatchard, *ibid.*, **47** (1925), 696.

one experiment that the maximum deviation in the liquid junction potential, of a junction established in this way, over a period of three days, was only two parts in three thousand, and a similar degree of reproducibility was obtained in almost every case.

The Theory of Liquid Junction Potentials.

Although the flowing junction has so high a degree of reproducibility, it is difficult to analyse the exact conditions which obtain within the actual mixed layer. Certainly, hydrodynamic effects due to surging of the liquids would be of some importance if the junction were formed near the top of the tube,¹ but even if these are absent, there will be electrokinetic effects between the two liquids and the walls of the vessel. At the point of formation in the flowing junction, the composition of the common layer is probably, at every point within the layer, a linear combination of the compositions of the extreme liquids or a so-called "continuous mixture layer."² But as the junction proceeds away from its origin down the side tube, free diffusion, which takes an appreciable time compared with the time for mixing, will take place to an increasing extent. This instability due to diffusion may be minimized by making the mixture layer very long, for the time taken for the steady state to be annihilated by diffusion is found to be directly proportional to the square of the distance throughout which the deviations were initially present.³ Assuming an idealised continuous mixture layer liquid junction (Fig. 75), in which neither hydrodynamical nor diffusion effects disturb the uniform change of concentration throughout the layer, the potential may be calculated from purely thermodynamic considerations.⁴ In such a transition layer between, for example, potassium chloride and hydrochloric acid, at an intermediate plane distant l from the pure liquid A (HCl), the concentration of A at all points in the plane will be x

¹ MacLogan, *Biochem. J.*, **23** (1929), 309.

² E. A. Guggenheim, *J. Amer. Chem. Soc.*, **52** (1930), 1317.

³ Bjerrum, *Z. Electrochem.*, **17** (1911), 58; corrected later, *J. Amer. Chem. Soc.*, **52** (1930), 1327.

⁴ Henderson, *Z. physikal. Chem.*, **59** (1907), 118; *ibid.*, **63** (1908), 325.

and therefore of B (KCl) will be $(c - x)$, where c represents the total concentration. At an adjoining plane distant $l + dl$ from the A side of the transition layer, the concentration of A will be $x + dx$ and of B will be $c - (x + dx)$. Within such an elemental sheet, the concentration may be supposed to remain sensibly constant, and it will therefore behave as a concentration cell across which there is a fall of potential $dE_{liq.}$. For hydrochloric acid and potassium chloride the valencies of all the ions are unity, and if, during the passage of one faraday of electricity across the elemental

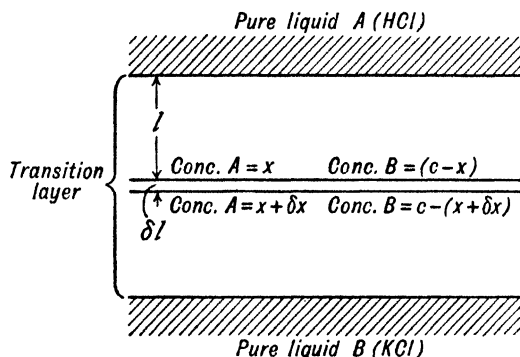


FIG. 75.—THE CONTINUOUS MIXTURE LAYER.

sheet, more substance is supplied to or taken from the surfaces in order to keep the concentration constant, we may write :

$$FdE_{liq.} = RT \sum n_{K+} d \ln a_{K+} . . . (421)$$

the n 's and a 's denoting the respective transport numbers and activities of the ions. It has been shown that, at least for mixtures of solutions of potassium chloride and hydrochloric acid, and probably for moderately dilute solutions of mixtures of the majority of uni-univalent electrolytes at the same concentration, the hypothetical individual activities of the ions are independent of the presence or nature of other ions in the solution.¹ Inside the transition layer therefore,

$$d \ln a_{Cl-} = 0 . . . (422)$$

¹ H. S. Harned, *J. Amer. Chem. Soc.*, **42** (1920), 1806.
Scatchard, *ibid.*, **47** (1925), 696.

and, since by definition, the transport number of an ion is the ratio of its mobility to the sum of the mobilities of all the ions :

$$\left. \begin{aligned} n_{\text{H}^+} &= \frac{\frac{x}{c}\lambda_{\text{H}^+}}{\frac{x}{c}\lambda_{\text{H}^+} + \left(\frac{c-x}{c}\right)\lambda_{\text{K}^+} + \lambda_{\text{Cl}^-}\left(\frac{x}{c} + \frac{c-x}{c}\right)} \\ n_{\text{K}^+} &= \frac{\frac{x}{c}\lambda_{\text{K}^+}}{\frac{x}{c}\lambda_{\text{H}^+} + \left(\frac{c-x}{c}\right)\lambda_{\text{K}^+} + \lambda_{\text{Cl}^-}\left(\frac{x}{c} + \frac{c-x}{c}\right)} \end{aligned} \right\} \quad (423)$$

From the property of the independence of ion activities in mixtures of solutions at equal concentrations, of potassium chloride and hydrochloric acid, the ratios of a_{H^+} to a_{H^+}' at two planes within the transition layer will be proportional only to the ratio of the concentrations x and x' at these planes. Thus :

$$\left. \begin{aligned} d \ln a_{\text{H}^+} &= d \ln \frac{x}{c} = \frac{c}{x} d\left(\frac{x}{c}\right) \\ \text{and } d \ln a_{\text{K}^+} &= d \ln \left(\frac{c-x}{x}\right) = -\frac{c}{c-x} d\left(\frac{c-x}{x}\right) \end{aligned} \right\} \quad (424)$$

Substitution in equation (421) from (423) and (424) now gives :

$$F dE_{\text{liq.}} = RT \frac{(\lambda_{\text{H}^+} - \lambda_{\text{K}^+}) d\frac{x}{c}}{\frac{x}{c}(\lambda_{\text{H}^+} - \lambda_{\text{K}^+}) + \lambda_{\text{K}^+} + \lambda_{\text{Cl}^-}} \quad (425)$$

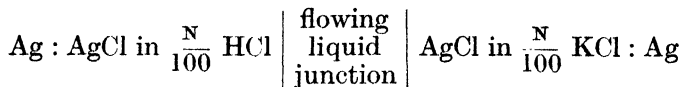
and the total liquid junction potential obtained by the integration of equation (425) throughout the whole transition layer is :

$$E_{\text{liq.}} = \int_{l=1}^{l=0} dE_{\text{liq.}} = \frac{RT}{F} \ln \frac{\lambda_{\text{K}^+} + \lambda_{\text{Cl}^-}}{\lambda_{\text{H}^+} + \lambda_{\text{Cl}^-}} \quad (426)$$

Errors arising from the variation in the mobilities with concentration are probably reduced by substituting the ratio of the molecular conductivities of the two salts in the logarithmic term

$$E_{\text{liq.}} = \frac{RT}{F} \ln \frac{A_{\text{KCl}}}{A_{\text{HCl}}} \quad (427)$$

and this formula is that most usually used¹ for calculating the liquid junction potential. It has been verified for solutions of hydrogen and potassium chlorides:² thus for the cell



since the potentials of the electrodes, which depend only on the chlorine ion activities are, at this concentration, sensibly the same, the measured potentials will be due to the liquid junction potential only. For $N/100$ solutions the observed potential is 0.0272 volt, that calculated from the Henderson formula (427) being 0.0274 volt. For $N/10$ solutions, where the potentials of the electrodes may still be assumed to be approximately equal and the measured E.M.F. still to be due almost exclusively to the liquid junction potential, the corresponding figures are 0.0278 volt and 0.0284 volt (calculated).

The continuous mixture layer such as is encountered approximately in the liquid flowing junction is not the only type of liquid junction which may be set up. From equation (421), which will apply to any elemental transition layer, in the general case of uni-univalent electrolytes, we have :

$$FdE_{\text{liq.}} = RT \sum_i n_i d \ln a_i \quad . \quad . \quad . \quad (428)$$

$$\text{i.e.,} \quad E_{\text{liq.}} = \frac{RT}{F} \int_1^n \sum_i n_i d \ln a_i \quad . \quad . \quad . \quad (429)$$

This equation allows the liquid junction to be defined at the limiting dilution, since here $a_i = c_i$ for every ion.³ Equation (429) cannot, however, be integrated at finite concentrations without a further knowledge of the variation of concentration along the transition layer. The value of $E_{\text{liq.}}$ calculated from it will therefore depend on the method by which the liquid junction is formed.⁴ If, instead of allowing free

¹ Lewis and Sargent, *J. Amer. Chem. Soc.*, **31** (1909), 363.

² MacInnes and Yeh, *loc. cit.*

Lewis, Brighton, and Sebastian, *J. Amer. Chem. Soc.*, **39** (1917), 2245.

³ H. S. Harned, *J. Physical Chem.*, **30** (1926), 433.

⁴ Guggenheim, *J. Amer. Chem. Soc.*, **52** (1930), 1317.

mixing, the two solutions are flowed past the opposite sides of a permeable collodion membrane stretched across the tube, then the composition of the liquid at all points on one side of the plane will be kept equal to that of solution I, and that at all points on the other side of a parallel plane will be equal to that of solution II. Diffusion from these artificially constrained planes will be free to take place between the planes until a steady state is reached. For this "constrained diffusion boundary," Planck solved the general equation (429) on the assumption that the mobilities of the ions were independent of the concentration and that the laws of ideal solutions were obeyed at the concentrations employed.¹ Strictly, therefore, the Planck transcendental equation will apply only when the solutions are at infinite dilution, and it cannot be applied with accuracy to the flowing liquid junction, where different conditions obtain from those assumed in its deduction. The values given, however, for the two types of liquid junction between solutions of potassium and hydrogen chlorides, in which the former is the denser, do not differ by more than one or two millivolts,² and as the concentration of the potassium chloride rises, the value of the overall liquid potential falls rapidly.³ It is therefore not surprising that a saturated solution of potassium chloride has always been useful in minimising liquid junction potentials.

In some recent measurements of activity coefficients⁴ the use of artificial liquid junctions between two different solutions has been avoided. The junction, which is here between solutions of the same solute is established in a concentration cell of the type,



by sliding the two halves of the cell over one another after the manner used in determining transport numbers by the

¹ Planck, *Ann. Physik*, **39** (1890), 161; **40** (1890), 561.

² Cumming and Gilchrist, *Trans. Faraday Soc.*, **9** (1913), 174.

Lewis, Brighton, and Sebastian, *J. Amer. Chem. Soc.*, **39** (1917), 2245.

³ Guggenheim, *ibid.*, **52** (1930), 1315.

⁴ MacInnes and Brown, *ibid.*, **53** (1931), 1356; *Chem. Rev.*, **18** (1936), 335.

moving-boundary method.¹ The junction so established between the two solutions is a "free diffusion boundary" (Guggenheim). Although in general the differential equation (429) cannot be solved explicitly from the stated conditions,² it has been shown, however, that in such a case when the two solutions forming the junction are the same, provided there are no heat effects due to mixing at the junction and that the mixed solutions do not react with the electrodes, the potential at the liquid junction is independent of the method by which it is formed.³ This would be expected from the general differential equation corresponding to (429), viz.:

$$E_{\text{liq.}} = \frac{RT}{zF} \int_1^n \sum_i n_i d \ln a_i$$

for when there are only two ionic species present, n_i and a_i are single-valued functions of the concentration for all mixtures of the two solutions forming the junction, and they are therefore independent of the method by which the two solutions are brought together.

Activity Coefficients Determined from Cell Measurements.

The most valuable determinations which can be obtained from measurements on concentration cells are of the activity coefficients of solutions at various concentrations. The use of the galvanic cell as a method for measuring these has these advantages over the osmotic methods, that the measurements are isothermal and that they may be carried out at any temperature and on any substance for which it is possible to set up a cell. With methods depending on the indirect osmotic properties, since the measurements are not isothermal, the calculations of the final values of the activity coefficients are complicated by the effects of the heat of dilution and of its temperature coefficient.⁴ Although the application of the E.M.F. method is limited to some extent by the difficulties of choosing electrodes reversible to the ion constituents of the cell, the measurements can be made

¹ MacInnes and Longworth, *Chem. Rev.*, **11** (1932), 171.

² P. B. Taylor, *J. Physical Chem.*, **31** (1927), 1478.

³ Scatchard and Buehrer, *J. Amer. Chem. Soc.*, **53** (1931), 574.

⁴ See Chapter VI, pp. 212, 213.

with a higher degree of precision and with much less labour than is possible when undertaking accurate determinations of the osmotic properties.

Such measurements can, however, never give any information about the individual ion activity coefficients, but only about their products. The value for the liquid junction potential

$$E_{\text{liq.}} = \frac{RT}{zF} \int_1^n \sum_i n_i d \ln c_i + \frac{RT}{zF} \int_1^n \sum_i n_i d \ln f_i \quad . \quad (430)$$

can only be found at finite concentrations when the transport numbers of every ion present are known as functions of the activity coefficients, and this information cannot be obtained by measurements on concentration cells. The definition of the liquid junction potential at any finite concentration where f_i is not unity would therefore require another arbitrary assumption, and although such an assumption has been made by referring individual ion activity coefficients to a standard state defined such that $f_{K^+} = f_{Cl^-}$ at all concentrations, the numerical values for the ion activity coefficients so obtained have no physical meaning.¹ The greatest care must therefore be observed when interpreting information obtained from measurements of concentration cells with transport.

Activity Coefficients from Concentration Cells with Transport.

The E.M.F. of a concentration cell between the concentrations c_1 and c_2 , where the mean activity coefficients of the solute are f_1 and f_2 , is given by

$$E = \frac{RT}{zF} \ln \frac{a_2}{a_1} = \frac{RT}{zF} \ln \frac{c_2 f_2}{c_1 f_1} \quad . \quad (431)$$

when there is no liquid junction in the cell, so that transport of the ion carrying the current cannot take place. In practice it is difficult to set up such cells without using an elaborate technique which limits the concentration range over which measurements can be made. It is much more common for half cells having the same ions, but with different

¹ Harned, *J. Physical Chem.*, **30** (1926), 433.
Guggenheim, *ibid.*, **33** (1929), 842.

concentrations of the solute, to be connected by a liquid junction which allows transport of the common ions to take place freely. By the passage of the cations and anions from one solution to the other, electrical work has been done which has not been included in the case of the cell without transport. This term may be evaluated using the free-energy principle : for if the difference between the E.M.F.'s of the same concentration cell, say of silver nitrate, arranged with and without transport be e , then, since the mobility of the nitrate ion exceeds that of the silver ion, the more dilute solution which takes on the charge of the faster moving ion, becomes negatively charged with respect to the stronger solution, and the rise in potential e is in the direction weaker to stronger solution. For the passage of F faradays of electricity, the extra change in free energy above that for the cell without transport is given by (346), viz. :

$$\Delta F = zeF$$

where a fraction n_+ of the total quantity of electricity passing is carried by the cations from the weaker to the stronger solution and the remaining fraction n_- is carried by the anions in the reverse direction. The corresponding isothermal reversible (and therefore maximum) work terms for the transference of these ions are therefore respectively :

$$\left. \begin{array}{l} n_+ RT \ln \frac{a_2}{a_1} \\ n_- RT \ln \frac{a_1}{a_2} \end{array} \right\} \quad . \quad . \quad . \quad (432)$$

and

$$\text{Thus} \quad \Delta F = zeF = n_- RT \ln \frac{a_1}{a_2} + n_+ RT \ln \frac{a_2}{a_1} \quad (433)$$

$$\text{and} \quad e = (n_+ - n_-) \frac{RT}{zF} \ln \frac{a_2}{a_1} \quad . \quad . \quad . \quad (434)$$

Equation (434) represents the contribution made to the E.M.F. of the cell by the transport of the ions, and the total E.M.F. of the cell with transport is therefore that of the concentration cell without transport together with the term e in (434), i.e. :

$$E_{\text{total}} = \frac{RT}{zF} \ln \frac{a_2}{a_1} (1 + n_+ - n_-) = \frac{2n_+ RT}{zF} \ln \frac{a_2}{a_1} \quad (435)$$

The deduction of this formula for the E.M.F. of a cell has neglected the change in transport number which occurs with the change in concentration due to the variations in the mobilities. This may be quite appreciable over the range c_1 to c_2 . In general, the transport number is a function of the concentration, so that :

$$E = \frac{2RT}{zF} \int_I^{II} n_+ d \ln a = \frac{2RT}{zF} \int_I^{II} n_+ (d \ln c + d \ln f) \quad (436)$$

The values of the transport numbers have been determined by the moving-boundary method with a high degree of accuracy over a range of concentration in a number of cases¹ and if equation (436) can be integrated, the values for the measurements of the E.M.F.'s in cells with transport can be used to determine activity coefficients. The method has been used by MacInnes and his collaborators² for those cases such as silver nitrate solutions where an electrode reversible to one of the ions (in this case the nitrate ion) cannot be obtained. In general, it is not possible to introduce into equation (436) expressions for E and n_+ in terms of the concentration, which are sufficiently simple to allow of a ready integration analytically. It is therefore necessary to integrate the equation graphically by substituting into (436) the transformation :

$$n_+ = n_+' + \Delta n_+ \quad . \quad . \quad . \quad (437)$$

n_+' being the value of the transport number at some reference concentration. Then

$$dE = \frac{2RT}{zF} (n_+' + \Delta n_+) (d \ln c + d \ln f) \quad . \quad . \quad (438)$$

$$\text{or} \quad \frac{zFdE}{n_+' 2RT} = d \ln c + \frac{\Delta n_+}{n_+'} d \ln c + d \ln f + \frac{\Delta n_+}{n_+'} d \ln f \quad . \quad . \quad (439)$$

¹ MacInnes and Longworth, *Chem. Rev.*, **11** (1932), 171.

Longworth, *J. Amer. Chem. Soc.*, **54** (1932), 2741; **57** (1935), 1185.

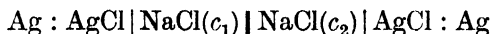
² Brown and MacInnes, *ibid.*, **57** (1935), 1356; *Chem. Rev.*, **18** (1936), 335.

Shedlovsky and MacInnes, *J. Amer. Chem. Soc.*, **58** (1936), 1970.

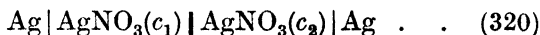
By integration between the limits I and II (439) gives

$$\Delta \ln f = \ln f_2 - \ln f_1 = \frac{zF\Delta E}{2n_+'RT} - \ln \frac{c_2}{c_1} - \frac{1}{n_+'} \int_I^{II} \Delta n \partial \ln c - \frac{1}{n_+'} \int_I^{II} \Delta n_+ \partial \Delta \ln f. \quad (440)$$

Of the terms in this equation, MacInnes and Brown obtain the values of $\frac{1}{n_+'} \int_I^{II} \Delta n_+ \partial \ln c$ by graphical integration, and the fourth term is evaluated by successive approximations, substituting first the values of $\Delta \ln f$ found by neglecting it (it is the term which has the smallest magnitude), and so obtaining a new set of values for $\Delta \ln f$. The measurements which have been made on sodium chloride in cells of the type



and on silver nitrate cells,



have completely confirmed the Hückel equation¹ for the variation of the activity coefficient with concentration, viz.

$$\ln f = - \frac{\alpha \sqrt{c}}{1 + \beta \sqrt{c}} + Dc$$

where β depends on the "distance of closest approach" of the ions (see p. 220). The measurements show that for both these salts the curves for $-\ln f$ against the square root of the concentration approach the correct limiting slope of $\alpha = 0.5056$ at 25° C. predicted by the simple Debye-Hückel theory (see Fig. 76). The method has also been applied to solutions of calcium chloride,² as a representative uni-divalent salt, and it is found, rather surprisingly that the Debye-Hückel equation applies in its simple form up to a molar concentration of 0.03 using a value 5.27 Å. for the closest distance of approach " r ." The extended Hückel equation can be used up to a concentration of 1.1. Comparative results by this method have, moreover, been

¹ Hückel, *Physikal. Z.*, **26** (1925), 93.

² Shedlovsky and MacInnes, *J. Amer. Chem. Soc.*, **59** (1937), 503.

obtained for hydrochloric acid solutions at 25° C.¹ and these are in excellent agreement with the results for this electrolyte from E.M.F. measurements in cells without a liquid junction.²

Activity Coefficients from Cells without Transport.

The activity coefficients of solutions of electrolytes may, however, be calculated more conveniently from E.M.F.

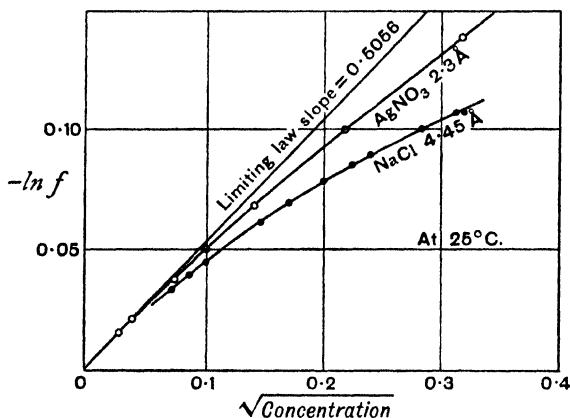


FIG. 76.—VARIATIONS OF $\ln f$ WITH $\sqrt{c}$ FOR SOME ELECTROLYTES.

measurements on cells in which transport of the electrolyte is not allowed to take place. Thus for the cell



no transport of any ion can occur and the E.M.F. must be due to the change in free energy resulting from the reaction :



Since the pressure at which the hydrogen is supplied is kept constant, the E.M.F. will therefore depend only on the concentration of the hydrogen chloride :

$$E = E^0 - \frac{RT}{F} \ln a$$

¹ Shedlovsky and MacInnes, *J. Amer. Chem. Soc.*, **58** (1936), 1970.

² Harned and Ehlers, *ibid.*, **54** (1932), 1350; **55** (1933), 652; 2179.

or, using the mean activity of the ions, $a_{\pm} = \sqrt{a}$:

$$E = E^0 - \frac{2RT}{F} \ln a_{\pm} \quad . \quad . \quad . \quad (441)$$

It should therefore be possible to calculate the activities of hydrochloric acid solutions directly from the E.M.F. measurements of this cell for different concentrations of hydrogen chloride. Lewis first showed how this could be done, by extrapolating the values of E in order to find E^0 .¹ In order to carry out such an extrapolation satisfactorily, it is necessary to have accurate data for the E.M.F.'s, particularly in the region of very dilute solutions, and it is, of course, especially in this region of concentration that the measurements are most uncertain:² Lewis' procedure is as follows. If (441) is changed to common logarithms, it becomes,

$$0.1183 \log a_{\pm} = E^0 - E$$

after substituting the numerical values for all the constants. This equation involves the activity, and to obtain the activity coefficient, $0.1183 \log c$ is subtracted from each side, giving

$$0.1183 \log \frac{a_{\pm}}{c} = 0.1183 \log f_{\pm} = E^0 - (E + 0.1183 \log c) \quad . \quad . \quad . \quad (442)$$

Now, at infinite dilution, $f_{\pm} = 1$, and hence $\log f_{\pm} = 0$. Also $c = 0$ so that the extrapolated value of the term $E + 0.1183 \log c$, at infinite dilution, obtained by the use of equation (442), is equal to E^0 , which is, of course, independent of the concentration. The value of $\log f_{\pm}$, and hence of the activity coefficient, can then be found for the corresponding value of E . The curve obtained in the plot is not linear, and even for an approximate extrapolation to be possible, measurements of the E.M.F. must be available down to the lowest concentrations. In this range, however, special precautions have to be taken in setting up the cells, since errors arising from adsorption of electrolyte at the

¹ Lewis and Randall, "Thermodynamics" (1923), pp. 263 *et seq.*, 332 *et seq.*

² Linhart, *J. Amer. Chem. Soc.*, 41 (1919), 1175.

electrodes and from solution of alkali from the glass, become too prominent to be neglected.¹

Even with these precautions in the experimental determinations of the E.M.F., the method of extrapolation is still too arbitrary to be satisfactory, and Hitchcock² first suggested employing the Debye-Hückel equation for the extrapolation so that the very uncertain values of the E.M.F.'s at the lowest concentrations, need not be used.

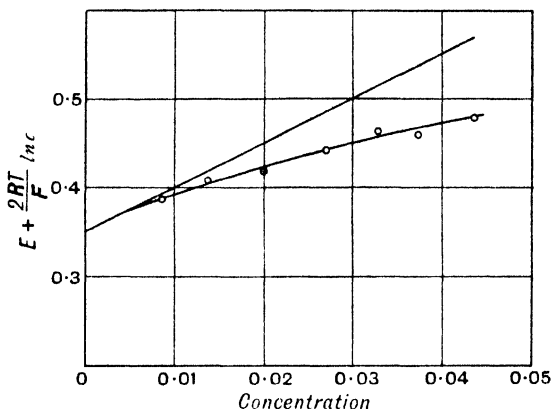


FIG. 77.—DETERMINATION OF ACTIVITY COEFFICIENTS FROM E.M.F. DATA.

Using a modification of the extended Hückel equation (320) for the activity coefficient, we may write

$$-\log f_{\pm} = 0.5056 \sqrt{c} - Bc$$

Substituting this into (442) gives

$$E + 0.1183 \log c - 0.1183 \times 0.5056 \sqrt{c} = E^0 - 0.1183 Bc$$

$$\text{or} \quad E^0 = E^0 \times 2kBc$$

From this equation, which is linear in c , an accurate extrapolation of the more accurate values of E determined at concentrations well outside the limiting range, may be made to give E^0 . This method is now widely employed for carrying out the extrapolations necessary in the determinations of activity coefficients, and measurements of the activities and

¹ W. R. Carmody, *J. Amer. Chem. Soc.*, **54** (1932), 188.

² D. Hitchcock, *ibid.*, **56** (1934), 2076.

other thermodynamic characteristics of hydrogen chloride, for example, by Harned and Ehlers¹ and by Åkerlof and Teare,² have been made using it, over a very wide range of concentrations up to the most concentrated solutions (16N).

Change of Activity Coefficient with Concentration.

The activity coefficient, which is of course unity at infinite dilution, decreases with increasing concentration, but for most substances rises rapidly above unity to quite high values after passing through a minimum. The results are

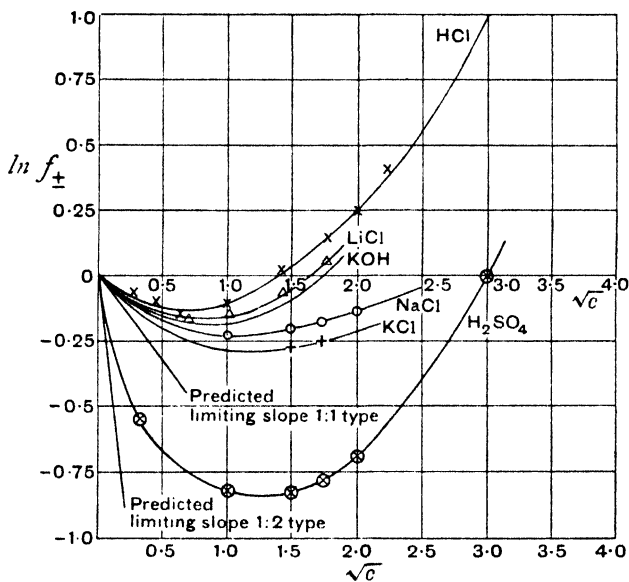


FIG. 78.—VARIATIONS OF $\ln f_{\pm}$ WITH $\sqrt{c}$ FOR SOME ELECTROLYTES AT HIGH CONCENTRATIONS.

best expressed by plotting $\ln f_{\pm}$ against the square root of the concentration, for according to the Debye-Hückel theory, the limiting slope of this curve should be the same for all electrolytes of the same valency type—e.g., for uni-univalent electrolytes, from equation (304),

$$\log_{10} f_{\pm} = -0.5056 \sqrt{c} \text{ at } 25^{\circ} \text{ C.}$$

¹ Harned and Ehlers, *J. Amer. Chem. Soc.*, **55** (1933), 2179.

² Åkerlof and Teare, *ibid.*, **59** (1937), 1855.

Fig. 78 illustrates the departure of the activity coefficient from the limiting law for the cases of a few common salts. The very large influence of the valency of the ions of the electrolyte (which occurs in the theoretical expression as a product) on the limiting slope is clear from the curve for sulphuric acid. The calculation of the activity coefficients of single salts from the E.M.F. data does not really provide a very good method for verifying the predictions of the unextended theory of interionic attraction, since, even with the extended method of extrapolation, the measurements cannot easily be made at concentrations so low that the theory is applicable with accuracy. Nevertheless, the activity coefficient curves do show that electrolytes of the same valency type exhibit the same behaviour in solutions.

At all ordinary concentrations where the limiting theory does not hold, the Hückel equation (320) :

$$\ln f_{\pm} = \frac{-\alpha\sqrt{c}}{1 + \beta\sqrt{c}} + Dc$$

may be applied, the values of the constants β and D being specific for each electrolyte. The linear term is here introduced to allow for the attraction of the solvent dipoles round the ions due to their intense electric fields. This corresponds to an effective repulsive force on ions of the opposite charge in the vicinity which would normally go to form the ion atmosphere. Moreover, there will be a lowering of the dielectric constant of the medium due to the electric saturation of the solvent in the immediate neighbourhood of an ion and both these effects are assumed by Hückel to be linear functions of the salt concentration.¹ The lowering of the dielectric constant of a solvent by the presence of a solute has been observed, but the results do not accord with the values of D required in these cases in order to make the observed values of the activity coefficient fit the equation.² But although Hückel's equation must be regarded as semi-empirical, it is very useful in interpreting activity data up to quite high concentrations, since when plotted it gives curves of precisely the same form as those observed, provided

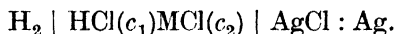
¹ Hückel, *Physikal. Z.*, **27** (1926), 411.

² Walden, Ulich, and Werner, *Z. physikal. Chem.*, **116** (1926), 260.

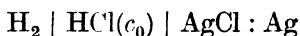
the correct choice of the constants is made. The mean ion activity coefficient will, of course, be altered if ions cease to behave as free particles due to their association in ion pairs, and the variations of $f_{\pm}$ with concentration therefore include the effects of the "true degree of dissociation" of the electrolyte.

Activity Coefficients in Mixtures of Strong Electrolytes.

The interionic attraction theory predicts that the mean activity coefficient of an electrolyte shall be a function only of the total ionic strength of the solution. It follows therefore that, over the limiting range, solutions of any electrolyte in the presence of a second electrolyte should show variations in the activity coefficient with the total ionic strength, of exactly the same form as for a single electrolyte in aqueous solution. At higher concentrations, however, the activity coefficients of one salt begin to depend on the nature of the other ions present. This behaviour has been illustrated from the measurements made by Harned¹ from cells of the type



in which the activity of the acid has been determined by comparison with the cell



The overall reaction in these cells, for the passage of 1 faraday, is the transfer of 1 gram-molecule of hydrochloric acid from the mixed solution to the pure solution—i.e. :



The E.M.F. for this process is

$$E = \frac{RT}{F} \ln \frac{a_{\text{H(salt)}} a_{\text{Cl(salt)}}}{a_{\text{H(acid)}} a_{\text{Cl(acid)}}} \quad . \quad . \quad (445)$$

$$\text{i.e.} \quad E = \frac{RT}{F} \ln \frac{\gamma_{\text{H(salt)}} \gamma_{\text{Cl(salt)}} c_1(c_1 + c_2)}{\gamma_{\text{H(acid)}} \gamma_{\text{Cl(acid)}} c_0^2} \quad . \quad (446)$$

¹ Harned, *Trans. Faraday Soc.*, **23** (1927), 462.

Harned and Åkerlöf, *Physikal. Z.*, **27** (1926), 411.

Harned in "Physical Chemistry," edited H. S. Taylor, 2nd edition, Vol. I, pp. 798 *et seq.*

$a_{H(\text{salt})}$ being the activity of the hydrogen ion in the salt solution. If the product $a_{H(c_2)}a_{Cl(c_2)}$ is known, it is therefore possible to calculate the activity product for hydrogen and chlorine ions in the mixed solutions. Measurements show that, for a given electrolyte in the presence of a number of homoionic salts, the curves all approach infinite dilution with the same limiting slopes, but that at higher concentrations the rule

$$\log f = -\alpha\sqrt{\mu} \quad . \quad . \quad . \quad . \quad (447)$$

ceases to hold, and the activity coefficient depends on the nature of the other ions present.

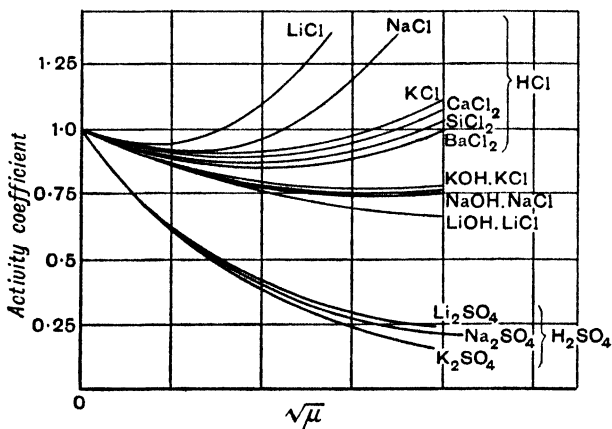


FIG. 79.—VARIATIONS OF ACTIVITY COEFFICIENT WITH IONIC STRENGTH IN MIXTURES OF ELECTROLYTES.

The variations of the activity coefficients from the linear law have been explained by the Hückel equation, although, as already mentioned, the linear term in his equation (320)

$$\ln f_{\pm} = -\frac{\alpha\sqrt{\mu}}{1 + \beta\sqrt{\mu}} + Dc$$

must be regarded as semi-empirical. For a mixture of two electrolytes at concentrations c_1 and c_2 , for which the total ionic strength is μ , it follows from (320) that, for the first salt

$$\begin{aligned}\ln f_1 &= \frac{-\alpha\sqrt{\mu}}{1 + \beta\sqrt{\mu}} + D_1c_1 + D_2c_2 \\ &= \frac{-\alpha\sqrt{\mu}}{1 + \beta\sqrt{\mu}} + (D_1 - D_2)c_1 + D_2(c_1 + c_2) \quad . \quad (448)\end{aligned}$$

and if the total ionic strength is kept constant, $(c_1 + c_2)$ is constant and

$$\ln f_1 = (D_1 - D_2)c_1 + \ln f_0 \quad . \quad (449)$$

This law of the linear variation of the activity coefficient with the concentration in a solution of constant total concentration has been verified up to quite high concentrations for hydrochloric acid in solutions of its salts.¹ At very low concentrations (less than 0.01M), the activity coefficient of hydrochloric acid in solutions of its salts at a fixed concentration becomes almost independent of its concentration. This may be seen by plotting $\log c_{\text{HCl}}$ against f_{HCl} where, by extrapolation, the values of the activity coefficients may be obtained down to zero concentrations. Together with similar measurements on hydroxide-salt cells and with a knowledge of the activity coefficient of the salt, it is then possible to obtain the ionic activity coefficient of water in salt solutions,² for the acid-halide cells give the product $f_{\text{H(0)}}f_{\text{Cl}}$, and the hydroxide-salt cells give the values $\frac{f_{\text{M}}f_{\text{OH(0)}}}{a_{\text{H}_2\text{O}}}$ at the same total concentrations of salt. In the expression $\frac{f_{\text{H(0)}}f_{\text{OH(0)}}}{a_{\text{H}_2\text{O}}} \cdot f_{\text{M}}f_{\text{Cl}}$ obtained by multiplying these, $\sqrt{f_{\text{M}}f_{\text{Cl}}} = f_{\text{MCl}}$, and at the very low concentrations, where the activity coefficient is independent of the concentration, $f_{\text{H(0)}}f_{\text{OH(0)}}$ may be replaced by $f_{\text{H}^+}f_{\text{OH}^-}$. The ionic activity coefficient product for water in salt solutions at different concentrations may therefore be obtained, and when plotted against the square root of the ionic strength of the salt, it is found to follow closely the analogous curves of activity coefficients in concentrated solutions (Fig. 80).

¹ Harned, *J. Amer. Chem. Soc.*, **48** (1926), 326.

² *Idem, ibid.*, **47** (1925), 930.

Harned and James, *J. Physical Chem.*, **30** (1926), 1060.

For the dissociation of water, we know that :

$$K = \frac{f_{\text{H}} f_{\text{OH}}}{a_{\text{H}_2\text{O}}} \cdot c_{\text{H}} c_{\text{OH}} \quad . \quad . \quad . \quad (450)$$

If the value of K is taken as 10^{-14} at 25°C. , values for the product $c_{\text{H}} c_{\text{OH}}$ and hence for c_{H} and c_{OH} in the salt solutions, may be obtained and the dissociation of water in salt solutions at various concentrations may be found. The variations of c_{H} and c_{OH} with the ionic strength will be in the reverse direction from the variation of f_{H} and f_{OH} , and, as

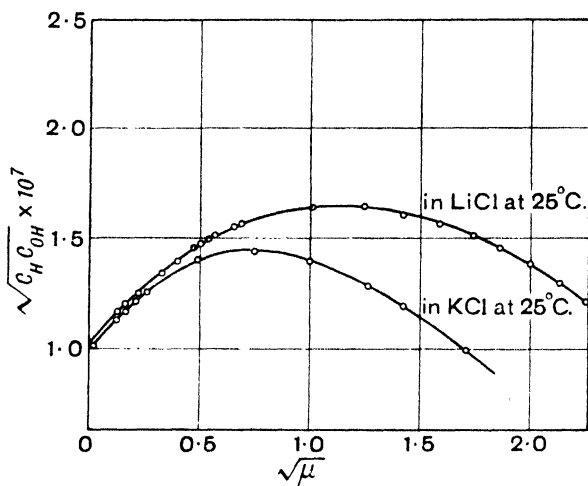


FIG. 80.—THE IONIC PRODUCT OF WATER IN SALT SOLUTIONS (Harned).

in the case of all weak electrolytes, the dissociation of the water is first increased by the addition of a salt. The increase in dissociation in dilute solutions follows from the decrease in the activity coefficients.¹ The variation of the water dissociation was predicted by Arrhenius from the changes in the catalytic activity of acetic acid caused by the addition of potassium chloride.

An interesting case showing deviation from the normal type of behaviour exhibited by weak electrolytes in the presence of salts at different concentrations, is provided by the indicator methyl orange, which is a sulphonic acid derivative.

¹ J. N. Brönsted, *J.C.S.*, **119** (1921), 574.

Using a colour absorption method, instead of an electrometric method, the dissociation constant of methyl orange determined at the optimum wave-length 5125 Å.U. where there is the greatest difference of absorption between the two colour forms, is found to be 3.34×10^{-4} at 18° C.¹ With this value, information has been obtained, by the same optical method, for the variation of the dissociation constant of acetic acid in the presence of sodium acetate at varying concentrations, and the results show that the method is capable of giving as accurate information about the deviations of the dissociation constants, as the more commonly used electrometric method. When, however, the variation of the dissociation of methyl orange itself in the presence of sodium acetate, is studied it is found that, although the limiting slope of the curve approaches that predicted by the interionic theory

$$\log f = -0.354\sqrt{2c}^2$$

and although the curve has the same general shape the rise of the dissociation constant begins at much lower salt concentrations than for other weak acids and always has a much higher value for the same salt concentration.³ This marked difference of behaviour may, however, be accounted for by the fact that methyl orange, or rather helianthin, shows a tautomeric equilibrium which in slightly acid

¹ N. V. Sidgwick, W. J. Warboys, and L. A. Woodward, *Proc. Roy. Soc., A*, **129** (1930), 537.

N. V. Sidgwick and L. A. Woodward, *ibid.*, A, **130** (1930), 1.

See also Güntelberg and Schiödt, *Z. Physikal. Chem.*, **135** (1928), 393.

The method was first used by H. T. Tizard, *J.C.S.*, **97** (1910), 2480.

² It is to be noted that a plot of $\log f = \log f_{H^+} f_{A^-}$ against $\sqrt{c}$ for strong acids gives a curve similar to that of $\frac{K_a}{K_e} = \frac{f_{H^+} f_{A^-}}{f_{HA}}$ in the case of weak acids, since f_{HA} is very small compared with $f_{H^+} f_{A^-}$.

³ See Fig. 81, where the values of

$$\frac{K_a}{K_e} = \frac{f_{H^+} f_{A^-}}{f_{HA}}$$

for methyl orange and for acetic acid are determined colorimetrically while the values for water and hydrochloric acid are found electrometrically. (Harned and Åkerlöf, *Physikal. Z.*, **27** (1926), 420.)

solutions is far over on the pseudo-acid (red-coloured) side (see Chapter XIII). For if this equilibrium between the true acid and pseudo-acid form is affected by the increasing salt concentration in such a way that more of the non-dissociated

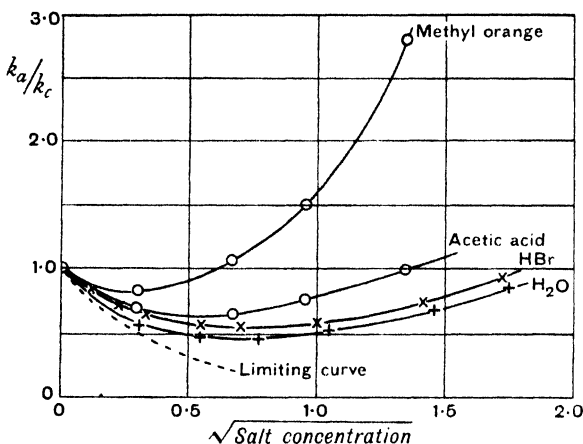


FIG. 81.—DISSOCIATION OF METHYL ORANGE AND ACETIC ACID IN SODIUM ACETATE SOLUTIONS.

(red) form is present at higher salt concentrations, the rapid abnormal rise of the curve with concentration is at once explained.¹

The Determination of Transport Numbers from Concentration Cell Measurements.

Jahn² in 1900 directed attention to the value of determinations of E.M.F.s in concentration cells as a means of interpreting the behaviour of strong electrolytes. By a comparison of ion concentrations found by E.M.F. data, in which variations of ionic velocities produce no effect, and from the conductivity values of the electrolytes at these concentrations, he showed that the ion velocities were not independent of the concentrations, as the simple Arrhenius theory supposed. MacInnes has used the measurements of concentration cells with and without transport as a means of determining this variation of the mobility with

¹ Sidgwick and Woodward, *loc. cit.*

² H. Jahn, *Z. physikal. Chem.*, 33 (1900), 345; *ibid.*, 35 (1900), 1.

concentration,¹ but the measurements are restricted to those cases in which the concentration cells can be set up without a liquid junction. Such a cell without transport $\text{Ag} : \text{AgCl}_{\text{solid}} | \text{MCl}(c_1) | \text{M}(\text{Hg})_x : \text{M}(\text{Hg})_x | \text{MCl}(c_2) | \text{AgCl}_{\text{solid}} : \text{Ag}$ may be set up either for a metal which can be easily amalgamated or for hydrogen by replacing the amalgam by a hydrogen electrode. Accurate measurements of these cells

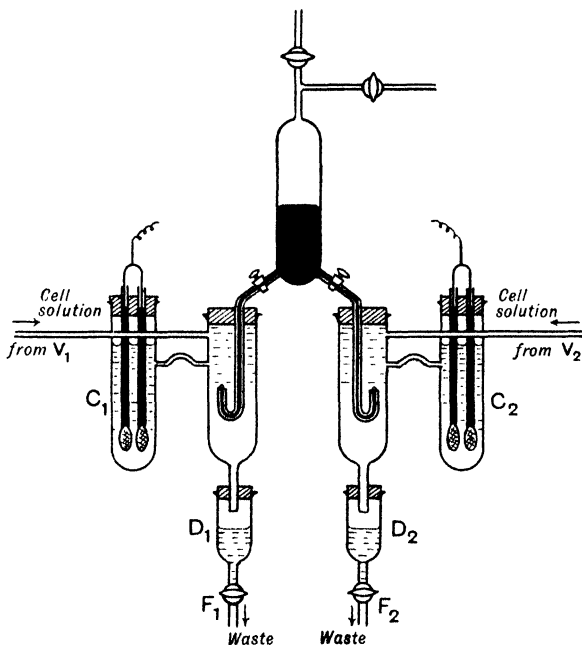


FIG. 82.—MACINNES-PARKER CELL FOR E.M.F. MEASUREMENTS WITHOUT TRANSPORT.

are, however, made difficult by the easy oxidisability of the amalgam, particularly when the metal is one of the alkali group. The same difficulty was encountered when determining the standard electrode potentials of the alkali metals in aqueous solutions, but it was found that an amalgam of one of these metals began to be attacked after only a short period of time had elapsed.² When the

¹ MacInnes and Beattie, *J. Amer. Chem. Soc.*, **42** (1920), 1117.

² Lewis and Kraus, *ibid.*, **32** (1910), 1459.

Lewis and Keyes, *ibid.*, **34** (1912), 119.

evolution of hydrogen began, however, the oxidative reaction at the surface accelerated. This oxidation could therefore be eliminated by the simple device of flowing the amalgam into the solution, so as to present a fresh surface from one instant to the next. If, similarly, the metal amalgam in the concentration cells is flowed from a reservoir through two fine capillary tubes into the two solutions containing the common ion which are themselves renewed, reproducible values for the E.M.F. can be obtained provided the solutions and amalgam are supplied and maintained free from oxygen. The arrangement illustrated, due to MacInnes and Parker,¹ has been used for measurements on the above cell where the common ion is sodium,² potassium, and lithium.³ Both

TABLE VIII.

E.M.F. Measurements in Lithium Cell, without Transport.

Concentration of LiCl solution in gram-mols. per 1000 c.c. of water.		Approximate conc. of amalgam.	E.M.F. in millivolts.
First solution.	Second solution.		
3.0	0.3	0.001%	141.71
		0.005%	141.69
0.3	0.03	0.005%	111.18
		0.002%	111.16
0.1	0.01	0.01%	110.57
		0.002%	110.55
		0.005%	110.53

the solutions, which are supplied from the closed reservoirs V_1 , V_2 , where they are stored in an inert atmosphere, and the amalgam are allowed to flow out into the air spaces D_1 , D_2 . From here they may be drawn off by means of the tubes F_1 , F_2 passing out of the bottom of the thermostat. The silver-silver chloride electrodes, which are kept away from the amalgam-solution junctions at C_1 and C_2 so that they may attain a stable equilibrium, require the greatest

¹ MacInnes and Parker, *J. Amer. Chem. Soc.*, **37** (1915), 1445.

² Allmand and Polock, *J.C.S.* (1919), 1020.

³ MacInnes and Beattie, *J. Amer. Chem. Soc.*, **42** (1920), 1117.

Lucasse, *J. Physical Chem.*, **30** (1926), 562; *Z. physikal. Chem.*, **121** (1926), 254.

care over their preparation, since the reproducibility of the E.M.F. measurements with these cells may be seriously affected if these electrodes contain inclusions in the chloride of small amounts of electrolyte at an unknown concentration.¹ Some of the results obtained with concentration cells of lithium chloride solutions using lithium amalgam to eliminate the liquid potentials, are given in Table VIII. The very small differences between successive readings, when the concentration of the amalgam is altered, is an index of the accuracy and reproducibility of the measurements with this design of cell.

The E.M.F. of a cell without transport is given by equation (371) as

$$E_1 = \frac{RT}{zF} \ln \frac{a_2}{a_1} \quad . \quad . \quad . \quad (451)$$

In order to obtain information about the transport numbers, it is therefore necessary to make observations on the values of the same cells arranged so that there is a liquid junction between the two solutions, across which transport may take place. Since, for a liquid junction established between two solutions containing the same ions at different concentrations, the value of the junction potential is probably independent of the method by which the two solutions are brought together, provided the mixed solutions do not reach the electrodes,² uncertainties due to the value of the liquid junction potential do not arise. The value for the E.M.F. of the cells with transport will be given by (436)

$$E_2 = \frac{2RT}{zF} \int_I^{II} n_+ (d \ln c + d \ln f) \quad . \quad . \quad (452)$$

when account is taken of the variation of the cation transport number with concentration. When the mean activity difference between the two solutions is small, the E.M.F. will be given by,

$$dE_1 = \frac{2n_+ RT}{zF} d \ln a \quad . \quad . \quad . \quad (453)$$

¹ R. H. Gerke, *J. Amer. Chem. Soc.*, **44** (1922), 1684.

W. R. Carmody, *ibid.*, **54** (1932), 188.

² Scatchard and Buehrer, *ibid.*, **53** (1931), 574.

Brown and MacInnes, *Chem. Rev.*, **18** (1936), 347.

This equation may be integrated graphically by the method already used for determining the activity coefficient, provided the transport numbers are known from independent measurements. Alternatively, an approximate value of the total E.M.F. may be found by carrying out measurements on concentration cells, in which one of the concentrations is fixed, and the other is increased by increments so small that, over each concentration range, the transport number may be regarded as sensibly constant. The E.M.F. of a cell having on one side a solution at the fixed concentration and on the other a solution at any concentration may then be found by summing the E.M.F.'s over each increment taken within this

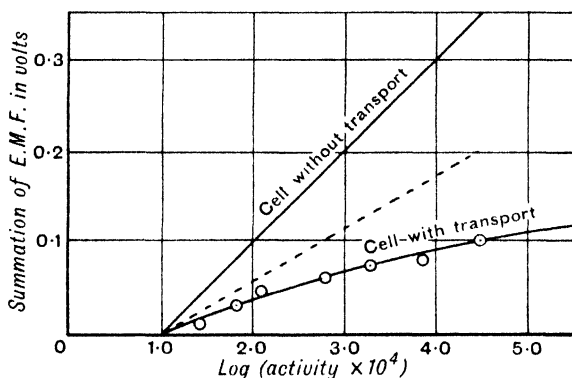


FIG. 83.—E.M.F. METHOD FOR ESTIMATING TRANSPORT NUMBERS.

range. In either case the E.M.F. plotted against the logarithm of the activity is not a straight line. The divergence from linearity will be a measure of the variation of n_+ with concentration. The value of the transport number at any concentration may therefore be estimated as the ratio of the E.M.F.'s of the cell with and without transport at that concentration (see Fig. 83) for if a small range of concentration dc around this chosen concentration be considered, then for the cells with and without transport respectively,

$$E_2 = \frac{2n_+ RT}{zF} d \ln a \quad . \quad . \quad . \quad (454)$$

$$E_1 = \frac{RT}{zF} d \ln a \quad . \quad . \quad . \quad . \quad (455)$$

i.e., from (454) and (455)

$$\frac{E_2}{E_1} = 2n_+ \quad . \quad . \quad . \quad . \quad . \quad (456)$$

The values which have been obtained by this method for the transport numbers of the lithium ion show fair agreement at some concentrations with the values determined by the Hittorf¹ and moving boundary methods² (see p. 129), but the complicated variations of the transport number with concentration are not correctly followed by the values determined by using this experimental method of integration.³ The accuracy, however, with which measurements of the E.M.F. may be made and the large number of them which are available make it certain that, if the results could be correctly interpreted, these measurements should give the most accurate of all values for transport numbers. In equation (436)

$$E = \frac{2RT}{zF} \int_1^{II} n_+ (d \ln c + d \ln f)$$

both n_+ and f are functions of the concentration, and the equation therefore could possibly be integrated analytically if both f and n_+ were expressed in terms of c . The Hückel equation (320)

$$\ln f = \frac{\alpha\sqrt{c}}{1 + \beta\sqrt{c}} + Dc$$

as has been shown, holds up to quite high concentrations, and may be substituted in the above expression, but no such simple function of c for the transport number can be found from theoretical considerations. Jones and Dole⁴ have made some measurements of transport numbers from determinations of the E.M.F. data by substitution in equation (436), and they find that n_+ may be represented as

$$n_+ = \frac{k_1}{1 + k_2\sqrt{c}} - 1 \quad . \quad . \quad . \quad (106)$$

¹ Noyes and Falk, *J. Amer. Chem. Soc.*, **33** (1911), 1436.

² Longworth, *ibid.*, **54** (1932), 2741.

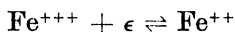
³ Jones and Bradshaw, *ibid.*, **54** (1932), 138.

⁴ Jones and Dole, *ibid.*, **51** (1929), 1073.

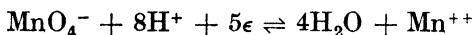
This is a purely empirical expression, which does not extrapolate to the correct limiting slope for the curve of n_+ against $\sqrt{c}$. From the E.M.F. data it is possible, using (436) to determine all the constants in the above equation, and so to estimate the values of the transport numbers at different concentrations. The results are in excellent agreement over the middle concentration range with the best values obtained by the moving-boundary and by the analytical methods (see Table III, p. 129).

Electropotential Measurements in Redox Systems.

The interpretation of measurements of the E.M.F.'s of reversible cells has offered a valuable means of elucidating some of the problems of both inorganic and organic chemistry. If an ion can exist in two states of oxidation, the higher state of oxidation is that which carries the greater positive charge. The addition of electrons to this, *e.g.*,



with the ferric ion, will cause the ion to pass into a lower state of oxidation—*i.e.*, to be reduced. The reactions are reversible and the law of mass action may be applied. The ions need not necessarily be derived merely by an alteration of the charge on the ion or radical, and indeed in many cases they are not “isomeric ions.” In the well-known reduction of potassium permanganate in acid solution



for example, the two ions differ in their states of oxidation by the combination of four oxygen atoms. If, into a solution containing two ions related as oxidation and reduction products, there is introduced an inert electrode, the electrons from this will take up an equilibrium with the electrons in the solution. The electrode therefore acts as an agent for the transfer of electrons between itself and the solution, and it will accumulate a charge of one sign or the other, depending on whether it supplies electrons at a greater or less rate than the reduced form of the radical or ion gives them up. This process is continued until the rates at which the forward and backward reactions proceed are equal. Obviously the

potential of the inert electrode will therefore depend on the position of the equilibrium between the two states of oxidation. Thermodynamically, the electrical work $z(E - E_0)F$ done in the oxidation of one equivalent of the lower radical at the electrode, against the potential difference $E - E_0$, which is supposed to exist between the electrode and the solution, is a measure of the change in free energy ΔF which takes place during the process. This may, in its turn, be expressed in terms of the concentrations of the components, or, more strictly, in terms of their activities, from equation (169) :

$$\Delta F = RT \ln K_a - RT \sum_v \ln a$$

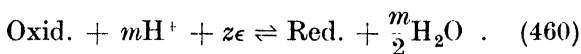
For unit reaction in which the reactants are initially at unit concentration and the products are finally brought to the same concentration (see p. 160) we therefore have :

$$zF(E - E^0) = -\Delta F = -RT \ln K_a \quad . \quad (457)$$

$$\text{or} \quad E - E^0 = -\frac{RT}{zF} \ln K_a \quad . \quad . \quad . \quad (458)$$

$$\text{i.e.,} \quad E = E^0 - \frac{RT}{zF} \ln K_c \quad . \quad . \quad (459)$$

where E_0 is the standard oxidation-reduction potential on the hydrogen scale. For the general oxidation-reduction reaction



equation (459) therefore becomes :

$$E = E^0 - \frac{RT}{zF} \ln \frac{(\text{Red.})}{(\text{Oxid.})(\text{H}^+)^m} \quad . \quad . \quad (461)$$

or for isomeric ions :

$$E = E^0 - \frac{RT}{zF} \ln \frac{(\text{Red.})}{(\text{Oxid.})} \quad . \quad . \quad . \quad (462)$$

A similar expression to this may be obtained from purely kinetic considerations without forgoing the discussion of the detailed mechanism of the process which the thermodynamic derivation cannot give.¹

¹ J. A. V. Butler, *Trans. Faraday Soc.*, **19** (1924), 734.

For every redox system of isomeric ions there must be an "equivalent hydrogen electrode" having the same potential as the system, since the potential of the hydrogen electrode can have any value depending on the hydrogen pressure. Although a pressure of hydrogen ions p_{H_2} , so

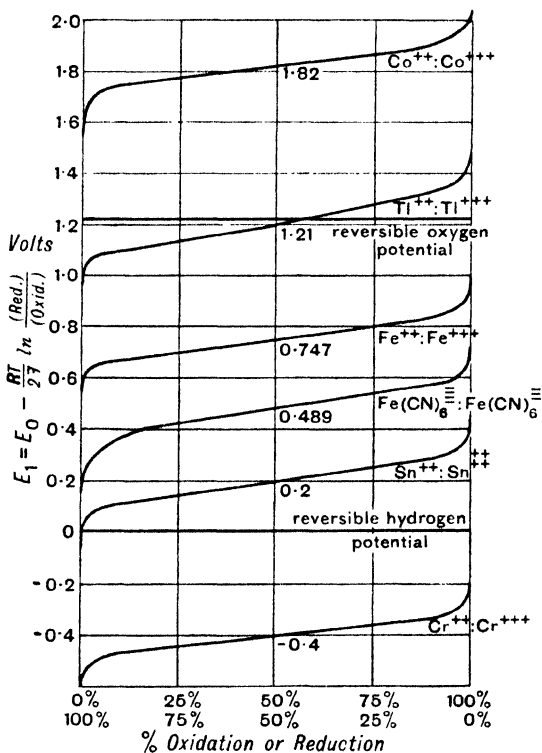


FIG. 84.—OXIDATION-REDUCTION CURVES FOR VARIOUS SYSTEMS.

low as must frequently be postulated to give the same potential

$$E = \frac{RT}{F} \ln \frac{a_{H^+}}{\sqrt{p_{H_2}}} \quad . \quad . \quad . \quad (463)$$

as the redox system, is not always molecularly possible, the concept is a useful one, particularly when dealing with the more complicated organic redox systems.

If the E.M.F. of an inert electrode immersed in a solution

containing isomeric ions be plotted against the ratio of the reduced form of the ion to the oxidised form, the curve obtained will in all cases be of the same form—viz., bilogarithmic.¹ Depending, however, upon the value of the standard oxidation–reduction potential E^0 , which is equal to E , when the activities of the two forms of the ions are equal, the curves will be displaced on the E.M.F. axis for each set of ions. On the diagram, the curves for several oxidation–reduction systems are included, and since the ratio (Red.)/(Oxid.) is here expressed as a percentage, the curves for every system are parallel to one another, a ten-fold change in the ratio (Red.)/(Oxid.) producing a change of 0.0591 volt in the E.M.F. of the inert electrode. Unfortunately the calculation of the standard oxidation–reduction potential from one set of conditions to another is complicated by the formation of complex ions, and the salt effect can, particularly in inorganic systems, change the activities of the ions sufficiently to render values for the standard potentials very tentative. It is therefore very necessary in any particular problem to discover, by making measurements at various concentrations and in various solvents, whether the use of concentration terms in place of activities is a sufficiently accurate approximation for the case in point² and the application of electrochemical ideas to these problems is therefore limited to some extent.

From the equation for the variation of the potential with the proportion of oxidant present, it is evident that a “pure” reductant has theoretically an infinitely low potential, and an oxidising or reducing agent must always be considered in terms of the proportion (Oxid.)/(Red.). The working range of a redox system will therefore be, for practical purposes, the straight part of the E -(% oxidant) curve—say from a system containing 1% of the reduced form to a system containing only 1% of the oxidised form. For a system in which only one faraday of electricity is exchanged per molar reaction, the change of E.M.F. from the mixture

¹ See the measurements of Peters (*Z. physikal. Chem.*, **26** (1898)) on the system $\text{Fe}^{++} : \text{Fe}^{+++}$ and of S. Popoff and A. H. Kunz, *J. Amer. Chem. Soc.*, **51** (1929), 382.

² J. Conant, *Chem. Rev.*, **3** (1926), 1.

containing 1% oxidant to that containing 50% oxidant will be approximately $-RT/F = -0.1182$ volt, and on the other side of the equimolecular mixture a similar change in E.M.F. will be produced by a change to a composition containing only 1% of reductant. The working range of the system may therefore, in this case, be considered as its standard redox potential ± 0.1182 volt. If the working range of two such systems overlap, they will interact with one another until the two systems have moved along their re-

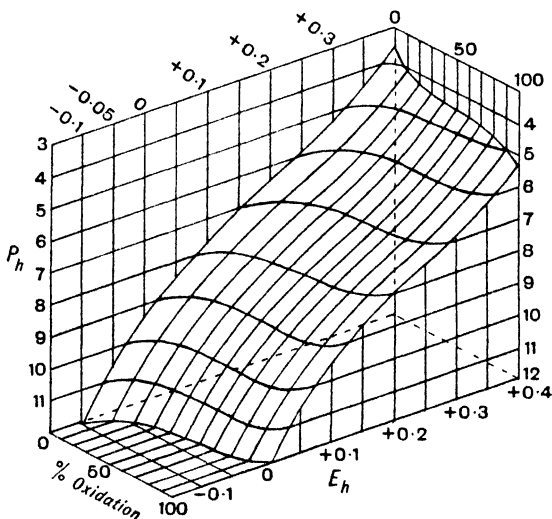


FIG. 85.—SURFACE $E \cdot pH \cdot \frac{[\text{Red.}]}{[\text{Oxid.}]}$ FOR 2 : 6-DIBROMOPHENOL-INDO-PHENOL.

spective curves to a common potential. Thus if a mixture of ferrocyanide and ferricyanide containing 95% of the former be titrated with a ferrous-ferric mixture containing 5% only of the former, the two equilibria react on one another and the proportion of ferrocyanide decreases at the expense of the increase in the ferric ion concentration until a new equilibrium is established where the two separate systems would have the same potentials.

In the more general case of oxidation reduction where hydrogen ions are involved, the equilibrium constant will depend on the hydron concentration—*e.g.*, for the general

reaction quoted above (p. 307), in accordance with equation (461)

$$E = E^0 - \frac{RT}{zF} \ln \frac{(\text{Red.})}{(\text{Oxid.})(\text{H}^+)^m}$$

In order to represent the system completely, a surface in three dimensions with $p\text{H}$, E and the ratio $(\text{Red.})/(\text{Oxid.})$ as its co-ordinates is therefore needed. Such a graphical representation (see Fig. 85) has been made for the system

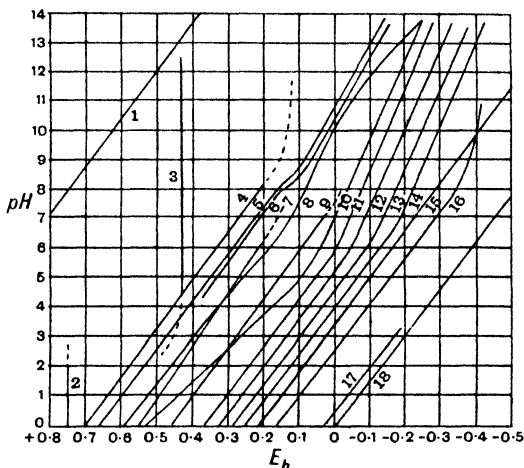


FIG. 86.—DIAGRAM OF $E/p\text{H}$ CURVES FOR VARIOUS REDOX SYSTEMS IN THE HALF-REDUCED STATE.

- | | |
|---|--|
| 1. Oxygen. | 10. Methylene blue. |
| 2. Ferric-ferro. | 11. Indigo tetrasulphonate. |
| 3. $\text{K}_3\text{Fe}(\text{CN})_6$. | 12. Indigo trisulphonate. |
| 4. Quinone. | 13. Indigo disulphonate. |
| 5. Phenol 2 : 6-dibromo-indophenol. | 14. Indigo monosulphonate. |
| 6. <i>m</i> -cresol-indophenol. | 15. 1 : 5-anthraquinone sulphonate. |
| 7. 1 : 2-naphthaquinone. | 16. β -anthraquinone sulphonate. |
| 8. Toluene blue. | 17. TiCl_4 . |
| 9. 1 : 4-naphthoquinone. | 18. Hydrogen. |

composed of 2 : 6-dibromophenol-indophenol and its reductant.¹ This may be reduced into one set of diagrams as in Fig. 86, all sections of the model, representing the variation of the potential with the $p\text{H}$ of the solution for a constant ratio of oxidant to reductant (say a ratio

¹ Clark *et al.*, *Public Health Reports*, **39** (1924), 804.
Clark, *Chem. Rev.*, **2** (1925), 127.

representing 50% oxidation), and another set, all of the type for the isomeric ion oxidation systems where the pH is kept constant and the electrode potential is represented as a function of the ratio (Red.)/(Oxid.). Two parallel lines, separated at all points by 1.227 volts (the reversible potential of the oxygen electrode), may be plotted on the E/pH diagrams, one for the hydrogen electrode, the other for the oxygen electrode in solutions of varying pH . The region below the line for the hydrogen electrode may then be identified with the region of hydrogen over-potential, and that above the upper straight line for the reversible oxygen electrode, with the region of oxygen over-potential. Between these two parallel lines lie the oxidation-reduction systems which are sufficiently stable not to decompose water to any appreciable extent.

Since the potential of the hydrogen electrode varies with the pressure of the hydrogen in accordance with equation (463), viz.:

$$E = \frac{RT}{F} \ln \frac{a_{H^+}}{\sqrt{p_{H_2}}}$$

it is obviously possible in all cases to superpose on the E/pH diagram for any particular redox system, two straight lines representing the variation of the reversible hydrogen potential with the acidity of the solution for two particular hydrogen pressures which will include the curve for the oxidation-reduction system between them. The expressions $\log 1/\text{hydrogen pressure}$ for these hydrogen pressures have been called the " rH " values for the system,¹ and only if the E/pH curves for the system were straight lines parallel to the hydrogen lines, could the system be characterised by one rH value. Usually therefore a range of rH values is necessary in order to define the system.²

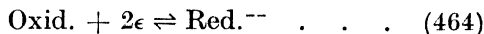
¹ L. G. Hewitt, "Oxidation-Reduction Potentials" [L.C.C. publications (1931), p. 14].

I. Barbaudy, *Chem. et Ind.*, 23 (1930), 14.

² Clark ("Determination of Hydrogen Ions," (1927), p. 387) has suggested that the term rH be discontinued, since it assumes a known relation to exist between E and the pH in which the system is measured, and it may therefore be somewhat misleading when applied to an incompletely studied system.

Organic Redox Systems.

An important special case arises in organic oxidation-reduction systems when the reductant is the anion of a dibasic acid, and a well-known example of this is the quinhydrone electrode which is used in the determinations of hydrogen-ion concentrations (see below). In this special case the essential reaction may be represented generally by



and the form $\text{H}_2 \text{Red.}$ from which the reductant is derived may dissociate in two stages for which the equilibrium constants are

$$\frac{[\text{H Red.}^-][\text{H}^+]}{[\text{H}_2 \text{Red.}]} = K_1 \quad . \quad . \quad . \quad (465)$$

$$\frac{[\text{Red.}^{--}][\text{H}^+]}{[\text{H Red.}^-]} = K_2 \quad . \quad . \quad . \quad (466)$$

The total concentration of all forms of the reductant is

$$[\text{RED.}] = [\text{Red.}^{--}] + [\text{H}^- \text{Red.}] + [\text{H}_2 \text{Red.}] \quad (467)$$

and since from (462)

$$E = E^0 - \frac{RT}{2F} \ln \frac{[\text{Red.}^{--}]}{[\text{Oxid.}]}$$

by substitution for the unknown quantities $[\text{Red.}^{--}]$, $[\text{H}^- \text{Red.}]$ and $[\text{H}_2 \text{Red.}]$ from (465), (466) and (467), (462) becomes

$$E = E^0 - \frac{RT}{2F} \ln \frac{[\text{RED.}]}{[\text{Oxid.}]} + \frac{RT}{2F} \ln [K_1 K_2 + K_1 [\text{H}^+] + [\text{H}^+]^2] - \frac{RT}{2F} \ln K_1 K_2 \quad (468)$$

When the ratio of oxidant to total reductant is kept constant and equal to unity, equation (468) simplifies to the form :

$$E = E^0 + \frac{RT}{2F} \ln (K_1 K_2 + K_2 (\text{H}^+) + (\text{H}^+)^2) - \frac{RT}{2F} \ln K_1 K_2 \quad (469)$$

The data for the redox potentials for solutions of different $p\text{H}$ may therefore be used to solve the equations for K_1 and

K_2 , the two dissociation constants of the acid H_2 Red. At high hydron concentrations only the term $(H^+)^2$, is of importance among the terms within the bracket—*i.e.*, (469) becomes :

$$E = E^0 + \frac{RT}{F} \ln (H^+) - \frac{RT}{2F} \ln K_1 K_2 . \quad (470)$$

which is of the same form as the equation for the hydrogen electrode. In acid solutions, therefore (*i.e.*, in solutions of low pH and high hydron concentration), a quinhydrone electrode, for example, will behave exactly as a hydrogen electrode, and may therefore be used for measuring the

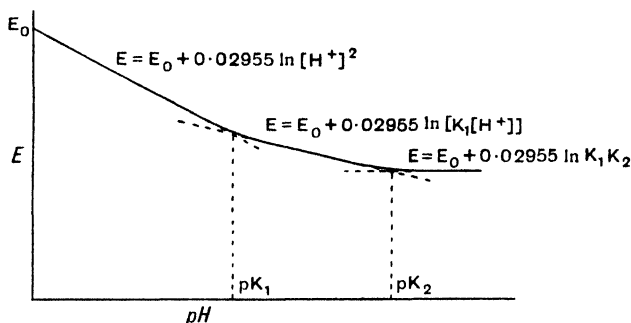


FIG. 87.—VARIATION OF POTENTIAL OF THE SYSTEM ANTHRAQUINONE-2:6-DISULPHONIC ACID AND ITS REDUCTANT WITH pH FOR THE RATIO $\frac{[Red.]}{[Oxid.]} = 1$.

hydron concentrations of unknown solutions, other factors being equal (see below). At low hydron concentrations only the first term $K_1 K_2$ of equation (469) will be prominent, and the potential will be independent of the hydron concentration. Between these is a section where $K_1(H^+)$ is the only important term—*i.e.*, where the potential is given by the expression

$$E = E^0 + \frac{RT}{2F} \ln K'(H^+) - \frac{RT}{2F} \ln K_1 K_2 \quad (471)$$

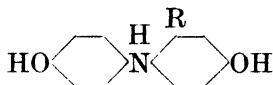
or
$$E = E^{0'} + \frac{RT}{2F} \ln (H^+) . . . \quad (472)$$

and over this portion of the E/pH curve, the slope $\partial E/\partial(pH)$ will be only half that in the region of higher hydron concentrations. The curve of E against the pH of the solution for the

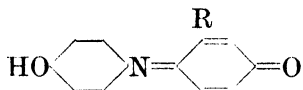
given ratio of oxidant to reductant will therefore have two points of inflection corresponding respectively with the pH s for $(H^+) = K_1$ and $(H^+) = K_2$. These are the pK values for the dibasic acid (see p. 376) from which the reductant is derived, and it is therefore possible to determine graphically all the equilibrium constants of the compound. The experimental results which have been obtained for anthraquinone 2 : 7-disulphonic acid show that the system obeys the general equation (468) accurately,¹ and that the slopes of the different sections of the E/pH curve agree with the predicted values—viz., -0.0591 , -0.02955 and zero respectively (see Fig. 87). In the well-known case of the oxidation of hydroquinone, which occurs at the quinhydrone electrode, the dissociation constants are, respectively,

$$K_1 = 1.75 \times 10^{-10} \text{ and } K_2 = 4 \times 10^{-12}$$

There is, however, the possibility of a complication in some cases due to the influence of the dissociation of substituent groups in the molecule. This effect does not arise in the anthraquinone disulphonic acid, but it becomes important in the substituted indophenol of which the reductant is :



and the oxidant :



The dissociation of the first form causes the dissociation constant of the common phenolic group to shift its value, and an extra term depending on the dissociation of the oxidant is therefore introduced into the equation for the electrode potential.²

¹ Conant, Kahn, Fieser and Kurtz (*J. Amer. Chem. Soc.*, **44** (1922), 1382).

² Clark, *Chem. Rev.*, **2** (1925), 143.

Cohen, Gibbs, and Clark, "Studies in Oxidation Reduction," Nos. IV, VI, and VII. *Public Health Rev.*, **39** (1924), 381, 804; **40** (1925), 649.

Many of these organic substances which have been described as oxidation-reduction systems are colourless in the reduced or leuco-form and strongly coloured in the oxidised state. In the presence of a solution which is more strongly oxidising than the substance—*i.e.*, which has a higher E/pH curve—the organic substance will pass almost completely into its coloured form, whilst with a solution of a substance entirely below its own rH range, it will be reduced to the colourless form. Provided therefore, the substance is suitable as an indicator¹—*i.e.* has a sufficiently high solubility, etc.—it may be used to estimate the redox potentials in the same way as acid-base indicators are used in determining the pH values of solutions. The methylene-blue system used as an indicator,² has been very fully investigated, for although methylene-white, the leuco-compound, is only very slightly soluble in neutral solutions, the dye is so intensely tinctorial that it may be used in very dilute solutions. Quite accurate determinations of the redox potentials of a solution are possible from estimations of the intensity produced by addition of the indicator solution to the system. Methylene blue may also be used as an indicator for the end-point of a titration of an oxidant by a reductant. Thus if Fehling's alkaline copper sulphate solution is titrated with aqueous glucose solutions in the presence of methylene blue, the end-point is indicated at once by the reduction of the methylene blue when the smallest excess of the glucose is present.

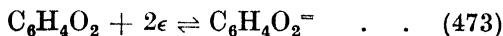
The Quinhydrone Electrode System.

We may now return for a moment to a consideration of the special case of the quinhydrone electrode, for its wide use in measurements of the hydron concentrations

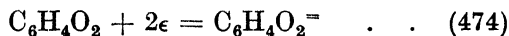
¹ See Clark and Perkins, *J. Amer. Chem. Soc.*, **54** (1932), 1228, who give reasons for rejecting the use of neutral red as a suitable indicator.

² Hirsch and Rütter (*Z. anal. Chem.*, **69** (1929), 193). Other systems which have been fully investigated include hæmoglobin-methæmoglobin (Conant and Fieser, *J. Biol. Chem.*, **62** (1925), 595) and the parahæmatin-hæmochromogen system (Conant and Tongberg, *ibid.*, **86** (1930), 733).

of solutions ¹ merits a discussion of both the theory and the practical details of the use of the electrode. The essential reaction taking place is the reduction of the quinone molecule to the hydroquinone ion :



and an inert electrode like platinum, immersed in the solution, will acquire a potential corresponding to this reaction. The reproducibility of the electrode is much improved by stirring the solution with nitrogen so that equilibrium conditions are attained very quickly,² and it is then possible, by flowing the liquid to be examined slowly through the cell, to obtain a continuous record of fluctuations in the hydron concentration. The value of the potential is very sensible to cracks in the glass into which the platinum is sealed, and considerable care has to be exercised in the method used for sealing in the platinum and annealing the glass around the joint, and subsequently in the methods adopted for cleaning and drying the electrode, to avoid recracking the seal so far as possible.³ The differences between the values of two electrodes, one with cracked glass, immersed in the same solution, may amount to as much as 0.1 volt. Crystals of quinhydrone which are sparingly soluble in aqueous solutions, keep the solution saturated with quinone and hydroquinone in constant proportions. At 25° the primary dissociation of the quinhydrone proceeds to the extent of about 93%. The reduction reaction



may therefore take place, followed by the formation of undissociated hydroquinone which may proceed in two stages as follows :

¹ E. Biilmann, *Ann. Chim.*, **15** (9) (1920), 109; *ibid.*, **16** (9) (1921), 324.

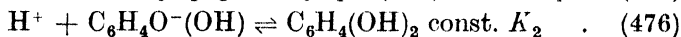
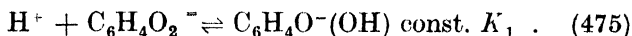
S. Veibel, *J.C.S.* (1923), 2203.

E. Biilmann, *Trans. Faraday Soc.*, **37** (1923), 676.

² Lammert, Morgan, and Campbell, *J. Amer. Chem. Soc.*, **53** (1931), 597.

Morgan and Lammert, *ibid.*, **53** (1931), 2454; **54** (1932), 910.

³ Biilmann and Jensen, *Bull. Soc. Chim.*, **19**; Morgan, Lammert and Campbell, *J. Amer. Chem. Soc.*, **53** (1931), 454.



It will be seen from equations (474), (475), and (476) that the quinhydrone redox system presents a special example of the general case for a system where the reductant is the anion of a dibasic acid. For the general case, equation (468) was derived. The E.M.F. of the electrode, corresponding to the reaction (474) will be given from equation (462) by :

$$E = E^0 - \frac{RT}{2F} \ln \frac{[\text{C}_6\text{H}_4\text{O}_2]}{[\text{C}_6\text{H}_4\text{O}_2^-]} \quad (477)$$

and since for reactions (475) and (476) we have

$$K_1 = \frac{[\text{C}_6\text{H}_4(\text{OH})\text{O}^-]}{[\text{C}_6\text{H}_4\text{O}_2^-][\text{H}^+]} \quad K_2 = \frac{[\text{C}_6\text{H}_4(\text{OH})_2]}{[\text{H}^+][\text{C}_6\text{H}_4\text{O}^-(\text{OH})]} \quad (479)$$

corresponding to (465) and (466), substitution for $[\text{C}_6\text{H}_4\text{O}_2^-]$ may be made in (477), giving

$$E = E^0 - \frac{RT}{2F} \ln K_1 K_2 - \frac{RT}{2F} \ln \frac{[\text{C}_6\text{H}_4(\text{O})_2][\text{H}^+]^2}{[\text{C}_6\text{H}_4(\text{OH})_2]} \quad (480)$$

$$= E^{0'} - \frac{RT}{2F} \ln \frac{[\text{C}_6\text{H}_4\text{O}_2]}{[\text{C}_6\text{H}_4(\text{OH})_2]} - \frac{RT}{F} \ln [\text{H}^+] \quad (481)$$

Now, in all but alkaline solutions the dissociation of hydroquinone is only very small—*i.e.*, the term $[\text{C}_6\text{H}_4(\text{OH})_2]$ in (481) may be put equal to the initial concentration of hydroquinone which is equal to the quinone concentration—*i.e.*,

$$E = E^{0'} - \frac{RT}{F} \ln [\text{H}^+] \quad (482)$$

On the hydrogen scale the constant E_0' has the value 0.6990 volt. As the concentration of hydrion decreases, however, the equilibria (474), (475), and (476) move more to the left-hand side, and the term $[\text{C}_6\text{H}_4(\text{OH})_2]$ cannot be put equal to the initial hydroquinone concentration. The electrode can therefore only be used for solutions on the acid side of neutrality. The deviations of the measured from the true values of the hydrion concentration in nearly neutral and acid solutions, are only about 0.5% at $\text{pH} = 6.25$

but they rise to 25% at $pH = 10.9$.¹ When the electrode is used for potentiometric titrations, therefore, the base is always added drop by drop to the acid so that the solution which is kept saturated with quinhydrone, is always on the acid side of neutrality until the end-point is reached. A further limitation to the use of the quinhydrone electrode arises from the fact that it cannot be employed in solutions like those containing sodium benzoate, which appreciably change the solubilities of quinone and hydroquinone, and so disturb the equality of their concentrations. Any oxidation-reduction system may also, by reducing some of the quinone, disturb this condition, and so introduce a "salt error" into the expression for the potential. But although fairly restricted in its range of usefulness, the quinhydrone electrode is extremely simple and efficient. Moreover, the equilibrium potential is attained very rapidly and, unlike the hydrogen electrode, where the platinum-black may easily be poisoned or so catalyse the reduction of a substance present, as materially to alter the system, the use of a quinhydrone electrode does not affect the solution, and it has therefore found wide applications in determining the hydron concentrations of many biochemical liquors.²

Irreversible Organic Redox Systems.

There are, however, only relatively few organic redox systems which are sufficiently stable to allow the reversible potentials to be measured easily, and in the great majority of cases no significant potentials can be measured, and the oxidation (as with aliphatic aldehydes in alkaline solutions) or reduction (*e.g.*, of dibenzoylethylene) is an irreversible process the inverse of which can never be observed experimentally.³ The potential of an inert electrode in such an unstable system will be subject to a drift with time as the result of some reaction which uses up either the oxidant or the reductant or both. These irreversible reductions may be expressed, at least qualitatively, in terms of a definite scheme

¹ V. K. La Mer and T. R. Parsons, *J. Biol. Chim.*, **53** (1923), 622.

² *J. Soc. Leather Traders Chemists*, **15** (1931), 367.

³ See Michaelis, "Oxidations-Reductions Potentiale" [Springer, Berlin, 1929], pp. 92-97.

of redox potentials unless the irreversible process is brought about in a heterogeneous medium, as in catalytic hydrogenation, when it is found not to be possible at all to treat the process from the electrochemical point of view.¹ The initial potentials of these systems may, in some cases where the drift of potential is only slight, be measured by extrapolating backwards to zero time the straight part of the curve representing the time variation of the potential of the solution of the reductant to which has been added an amount of oxidising agent estimated to produce a certain quantity of oxidant.² But in general, if an intermediate redox system, having a high degree of instability is produced, as with the monatomic phenols and amines, where the oxidant is a free radical,³ Conant's method of "potentiometric indicators" may be used to give an approximate value for the potential of the system.⁴ If to a stable reversible redox system, such as that of hydroquinone-quinone, the potential of which is sufficient to oxidise the substance being investigated, is added a small quantity of a substance which does not reduce reversibly in homogeneous solution, this will cause a change in the potential of the system due to the disappearance of some of the oxidant form from the reference system. The change in potential of the reference system (which must have been chosen as one which comes rapidly to equilibrium) therefore indicates the extent to which oxidation has taken place in the unknown system. The highest potential at which "appreciable reduction" will take place under the conditions of the experiment is termed by Conant, the "apparent reduction potential."⁵ By using a series of redox systems carefully chosen to have a convenient range of potentials, its value for any particular compound may be approximately determined to within

¹ Conant, *Chem. Rev.*, **3** (1926), 1.

² L. F. Fieser, *J. Amer. Chem. Soc.*, **52** (1930), 4915.

³ *Idem, ibid.*, **52** (1930), 5201.

⁴ Conant and Lutz, *J. Amer. Chem. Soc.*, **45** (1923), 1047; **46** (1924), 1254.

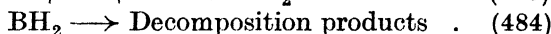
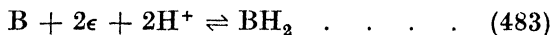
Conant, *Chem. Rev.*, **3** (1926), 1.

⁵ Conant and Lutz, *loc. cit.*

Conant and Pratt, *J. Amer. Chem. Soc.*, **48** (1926), 2468, 3178, 3220.

25 mv., which is a sufficient degree of accuracy to enable a consistent account of irreversible reduction to be developed.

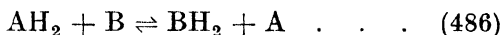
In order to account for the time variations of the potentials of these homogeneous irreversible systems, Conant supposes the reduction to take place in two stages, represented in general by



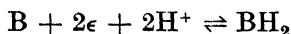
The first of these is a reversible reaction in every way analogous to the reversible redox systems like that of hydroquinone-quinone; the isomerisation process (484) is, however, irreversible, and takes place at a rate given by

$$-\frac{\partial(BH_2)}{\partial t} = K[(BH_2) - x] \quad . \quad . \quad . \quad (485)$$

When a reversible reducing system such as the quinone-hydroquinone system (represented here as A/AH_2) is being used to effect the reduction of B in (483) the reaction



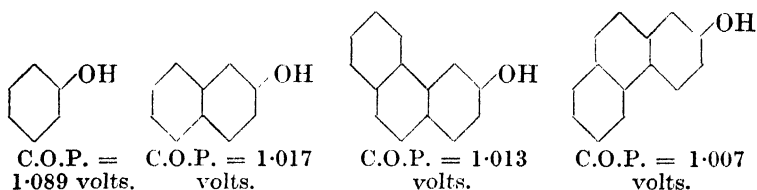
will proceed at just the same rate as the isomerisation process in order to compensate the removal of BH_2 from the equilibrium. Thus the process observed is governed by the relatively slow reaction (486) depending on (BH_2) and K (of equation (485)) and therefore depending on the difference between the potentials of the irreversible reducing system and the reversible stage of the irreversible process (484). The variations with the hydrogen-ion concentration which have been observed in the apparent reduction potentials, follow curves which show much the same characteristics as a reversible redox system under similar conditions. This fact appears to verify the conclusion that the cause of the irreversible reductions is largely determined by some reversible reduction process of the type,



similar to that which takes place with the quinones, followed by an irreversible reaction.

The concept of an irreversible apparent reduction or oxidation potential is admittedly vague, but since the rate

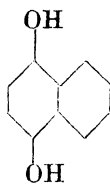
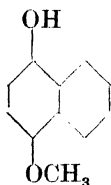
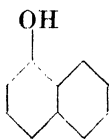
of the reaction depends, in part at least, on the potential of the reference system, it should be possible, by the suitable adjustment of the chosen reference system, to bring the reduction or oxidation process practically to a standstill, at which point the rate factor would no longer appreciably influence the potential. Fieser prefers to use a "critical oxidation potential" in place of Conant's apparent oxidation potential, since this may be determined experimentally with a higher degree of accuracy.¹ Since, however, there is no potential at which a reaction comes completely to a stop, the critical oxidation potential depends both on the potential of the reference system and on the rate factor, and therefore fulfils the requirement of a constant needed to characterise a series of substances. During the measurement of the critical oxidation potential, however, the rate is made very small, and the rate factor must therefore be exceedingly small. Great interest attaches to the fact that the critical oxidation potential is, to a large extent, a structural property having approximately the same value for a series of substances closely related to one another; thus



It is therefore possible from measurements of this quantity to determine, for example, whether the oxidation of two substances which appear to be formally related, proceeds by the same mechanism in each case. Catechol would be expected to have a critical oxidation potential very close to that of guaiacol if the oxidation involved only one single hydrogen atom and the formation of a univalent radical. The large difference in the normal potentials of the two compounds—viz., 0.742 for catechol and 0.808 for guaiacol—must mean that the oxidations follow different mechanisms in the two cases, probably involving the formation of a transitory orthoquinone in the case of the unsubstituted

¹ Fieser, *J. Amer. Chem. Soc.*, **52** (1930), 5204.

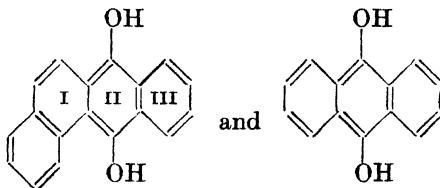
compound. An even more striking example of the elucidation of the mechanism of oxidations in hydroxy-compounds from these electrochemical studies occurs in the case of the naphthalene derivatives. The substitution of a methoxy-group (used to protect an -OH from oxidation) in the five position of α -naphthol alters the critical oxidation potential practically not at all, whereas the potential of 1:5-dihydroxy-naphthalene is 0.124 volt below that for α -naphthol.



C.O.P. = 0.797 volt. C.O.P. = 0.792 volt. C.O.P. = 0.673 volt.

It may therefore be safely assumed that in the dihydroxy-compound the oxidation proceeds by the formation of a transitory quinone, and not by the same mechanism as is followed by α -naphthol.¹

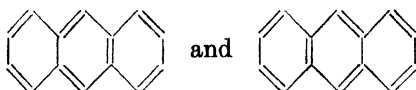
Considerable light has been thrown on the structure of anthracene from an investigation of the reduction potentials of some of its derivatives.² The abnormally low reduction potential of anthraquinone is an index of the unusual reactivity of the anthracene nucleus, which might be due either to an *ortho*quinonoid grouping of the double bonds or possibly to the existence of a *para* bond between the *meso* positions. Assuming the *ortho*quinonoid structure, the potentials of the systems derived from



¹ See also Fieser, *J. Amer. Chem. Soc.*, **51** (1929), 2480.
Fieser and Peters, *ibid.*, **53** (1931), 793.

² Fieser and Ames, *ibid.*, **49** (1927), 2611.
Fieser and Dietz, *ibid.*, **53** (1931), 1128.
Cf. Fieser and Lothrop, *ibid.*, **58** (1936), 769.

should differ only by an amount depending on the addition of the phenylene group, provided there is no modification in the structure of the anthracene nucleus in the 5:6-benzanthraquinone. This assumes that the addition of the phenylene group does not influence the behaviour of anthracene towards oxidation at all, but it is reasonable to suppose that the addition of the extra ring will have a stabilising influence on the *o*-quinonoid group, thus decreasing its tendency to undergo oxidation. The increment in the oxidation potential due to the added phenylene group may be found from the naphthalene and phenanthrene compounds to be 40 mv. In the anthracene compounds the difference between the potentials is 73 mv., but the extra increment is attributed to the stabilisation of the *o*-quinonoid system of the reductant. A second phenylene group added to the nucleus III of the mono-benzo-compound should, however, only have the normal effect of 40 mv., since this second added nucleus cannot further stabilise the *o*-quinonoid grouping, and this is in fact observed experimentally. A symmetrical anthracene structure would require the effect of both phenylene nuclei to be the same when added to the benzene groups I and III, and it must therefore be supposed that anthracene has the *ortho*quinonoid structure or rather that it is a resonance hybrid of the two possible unsymmetrical structures



This conclusion is supported by an X-ray examination, which reveals that all the carbons in the molecule are practically coplanar, so that a *para*-link would have to be almost twice as long as any other known carbon-carbon linkage.¹

¹ W. H. Bragg, *Proc. Physical Soc.*, **34** (1921), 33.

CHAPTER X

IRREVERSIBLE ELECTRODE PROCESSES

Polarisation and Over-voltage.

It has long been known that if acidulated water be electrolysed between two brightly polished platinum electrodes, practically no electrolysis takes place until a certain critical voltage has been overcome by the applied E.M.F. If to such a cell an external E.M.F. be applied, no current is observed to flow at first, due to the negative effect of the back E.M.F. But as the applied E.M.F. is gradually increased, so that of the cell rises up to a certain critical value, and before electrolysis can take place this critical potential must be exceeded.¹ This E.M.F. is known as the decomposition potential of the electrolyte, and if a total E.M.F. E be applied to the cell, Ohm's law is obeyed only if E is replaced by the effective E.M.F. $E - e$, where e denotes the decomposition potential *i.e.* :

$$E - e = cR \quad . \quad . \quad . \quad . \quad . \quad (487)$$

If E exceeds e by any appreciable amount, a finite current passes through the cell and causes electrolysis to take place, and since this process cannot be reversed by diminishing the applied E.M.F., the cell becomes irreversible due to the "polarisation" of the electrodes. The difference between the potential of an electrode which has become polarised and the reversible potential of that electrode in a solution of the electrolyte of the same concentration, is called the over-voltage of the electrode. This will therefore be equal to the E.M.F. of the cell

Metal : H_2 (depositing) | H^+ | H_2 (reversible) : Pt
and the hydrogen over-voltage of a metal will therefore depend upon the metal itself.

¹ Newbery, *J.C.S.* (1914), p. 419.

Polarisation in this sense has long been associated with the deposition of hydrogen bubbles on the electrode, but there is another and entirely different type of polarisation which may arise during electrolysis due to the changes in concentration of a common ion at the electrodes. Normally, in measurements of the E.M.F. of reversible cells, so little current is allowed to pass that changes in concentration in the vicinity of the electrodes are negligible. If, however, in a cell of the type



in which initially there is no back E.M.F., a heavy current is passed, there is a change in the concentration of Ag^+ ion at the electrode, and the concentration cell produced by the electrolysis sets up a counter E.M.F. the magnitude of which depends on the difference between the concentrations, and therefore on the current density applied to the cell. If the applied E.M.F. is removed, this concentration polarisation will slowly disappear, due to the diffusion of the electrode liquids into the solution. This process of mixing may be hastened, and therefore the back E.M.F. set up during the electrolysis may be reduced, by vigorous stirring.¹ Dolezalek² has attributed the variations in the E.M.F. of the lead accumulator during discharge when the potential falls from about 2.01 volts, first rapidly to 1.9 volts, then slowly to about 1.8 volts, followed on standing by recovery to its initial value of 2.01 volts, solely to the effects of concentration polarisation in which sulphuric acid accumulates at the electrodes during the charging process and is prevented by the porous lead dioxide from diffusing quickly.

Measurement of the Over-voltage.

The first measurements of over-voltage were made while continuous current electrolysis was taking place as evidenced by the visible liberation of hydrogen. Tafel concluded from measurements on a number of cathodes in dilute sulphuric acid, which were used in conjunction with a platinum anode,

¹ F. G. Cottrell, *Z. physikal. Chem.*, **42** (1903), 385.

² "Theory of the Lead Accumulator," Dolezalek, trans. von Emde (New York, 1910).

that if V be the cathode potential and i the current density, these quantities were related by the relation

$$\epsilon = a + b \log i \quad . \quad . \quad . \quad (488)$$

or

$$i = Ke^{-\alpha V} \quad . \quad . \quad . \quad (489)$$

where a and b or α and K are constants at a given temperature.¹ The numerical value of α is found to be

one half the factor $\frac{F}{RT}$. During continuous electrolysis,

however, the nature of the electrode may be changed, and observations have shown that the magnitude of the polarisation depends on the previous history of the electrode.²

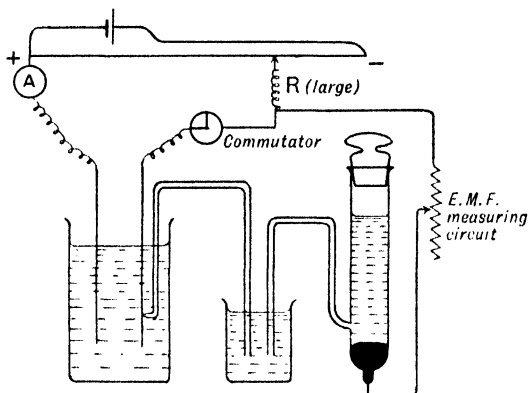


FIG. 88.—NEWBERY'S METHOD FOR MEASURING OVER-VOLTAGE.

It is therefore desirable to eliminate these complicating effects during the measurement of the over-potential. This may be achieved by using a commutator which will alternately make and break the circuit used to supply the applied E.M.F.³ A large resistance R is included in the circuit providing the electrolysing current, so that any changes in the

¹ Tafel, *Z. physikal. Chem.* **50** (1905), 641; **50** (1906), 712. This relationship has been confirmed by Lewis and Jackson, *ibid.*, **56** (1906), 193, and recently by Harker and Adams, *ibid.*, **29** (1925), 205, and Bowden and Rideal, *Proc. Roy. Soc., A*, **121** (1928), 59.

² For criticisms of the continuous current method, cf. MacInnes, *J. Amer. Chem. Soc.*, **41** (1919), 2013; **42**, (1920), 2223; Newbery, *ibid.*, **42** (1920), 2007.

³ Newbery, *J.C.S.* (1914), 2419; (1916), 1051, 1067, 1107; Pring and Tainton, *ibid.* (1914), 721.

resistance of the electrode will only slightly influence the current passing. Moreover, the connecting tube for the standard element must be brought very close to the electrode the over-potential of which it is required to measure, in order to minimise the effect of a fall of potential towards the electrolyte produced by the passage of a current through it. Newbery arranged a circuit (Fig. 88), in which, at the same time as the applied E.M.F. was broken, the cathode was connected into a circuit enabling its potential to be measured against a standard hydrogen electrode. The results obtained with this arrangement were invariably lower than those by the continuous current method, probably due to the effect of an alternating induced current set up by the make and break of the intermittent circuit.

The Development of Over-voltage.

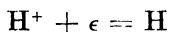
The fact that the earliest measurement of over-voltage revealed that the magnitude of the effect depended on the nature of the surface, naturally led to the view that over-voltage was in some way connected with the formation of gas at the electrodes.¹ Newbery's results showed that, using brightly polished platinum electrodes, the passage of a heavy current for a short time caused the surface to become dulled, and that this blackening, as revealed by a microscopic examination, consisted of minute pittings in the metal, which suggested that the surface of the metal had been blown up from within by the escape of adsorbed hydrogen as a gas. He attributed over-voltage partly to the formation of unstable hydrides of high electrical conductivity at the electrode surfaces. The dependence of over-voltage on the valency then followed from the fact that multivalent elements can form more than one hydride and can therefore have more than one over-voltage.² It is more probable, however, that these "hydrides" consist only of adsorbed layers of hydrogen atoms possessing a special orientation with respect to the surface since much of the evidence adduced for the existence of these hydrides has been shown

¹ G. Pring, *Z. Electrochem.*, **6** (1913), 255.

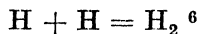
² MacInnes and Adler, *J. Amer. Chem. Soc.*, **41** (1919), 194.
MacInnes and Contieri, *ibid.*, **41** (1919), 2013.

to be equally compatible with the view that the effects are due to very small quantities of negative metal impurities which deposit on the cathode during electrolysis.¹ The remaining part of the total over-voltage was supposed to arise from a "transfer resistance" set up by the formation of an obstructive film of material at the electrode which impeded the passage of a current,² this fraction of the over-potential varying in an irregular manner with the current density. Bowden³ has demonstrated, however, that the transfer resistance effect which Newbery observed was almost certainly due to the presence of dissolved oxygen and metal ions in the cathode vessel. For, if these were rigorously excluded, the decay of the over-potential was slow, and could be followed from the moment of opening the circuit. The view that over-voltage arose from the accumulation of gas at the surface of the electrode received some confirmation from measurements of the over-voltage of hydrogen on platinised platinum using very low current densities.⁴ Here a periodicity in the over-voltage was noticed, the rise being associated with the separation of each bubble of gas and the fall with the growth of the nucleus left by the separation of the bubble.

The exact mechanism by which the accumulation of gas at the electrodes can give rise to an over-voltage depends on whether we regard the essential rate or controlling factor as the accumulation of an electromotively active film of hydrogen ions followed by neutralisation of these ions :



as supposed by Nernst,⁵ or as the further stages in which the discharged ion is transformed into the gaseous product of electrolysis—*e.g.* :



Any factor which retards whichever of these reactions is the critical process, will increase the over-voltage, since there

¹ Bowden, *Trans. Faraday Soc.*, **23** (1927), 571.

² Newbery, *Proc. Roy. Soc.*, **107** (1925), 486; **129** (1928), 680.

³ F. P. Bowden, *ibid.*, **126** (1929), p. 107.

⁴ See also Heyrovsky, *Trans. Faraday Soc.*, **19** (1934), 785.

⁵ Nernst, *Ber.*, **30** (1899), 1547.

⁶ Bancroft, *J. Physical Chem.*, **20** (1916), 396.

will be an accumulation at the electrode of atomic hydrogen at a faster rate than this can combine into molecules. The potential would then depend on this film of atomic hydrogen, and would not be that of the hydrogen electrode under normal conditions.

Rates of Development and Decay of Electrode Potentials.

Recently the problem of over-voltage has been reinvestigated by kinetic studies of the establishment and decay of electrode potentials. The commutator method of

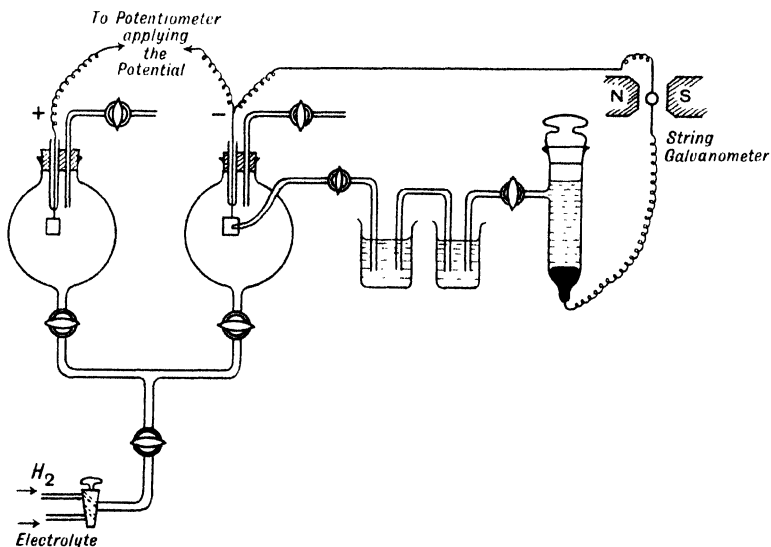


FIG. 89.—BOWDEN AND RIDEAL'S APPARATUS FOR MEASURING THE GROWTH AND DECAY OF THE OVER-VOLTAGE.

measuring the over-potential is unsuited to the measurement of the change in electrode potential during the establishment of a layer of electromotively active material on the electrode, since it only allows the observation of the average of a large number of cycles, and not of the initial growth and decay. The best results in the actual measurements have been obtained using a string galvanometer, since this does not draw an appreciable current from the test electrode.¹ In order to keep both the electrodes and the solutions free from

¹ F. P. Bowden and Rideal, *Proc. Roy. Soc.*, **120** (1928), 59.

oxygen, the cells are arranged so that they can be evacuated and filled with hydrogen and the oxygen-free electrolyte blown in under the pressure of the hydrogen. Observations made with this arrangement (Fig. 89) have revealed that, provided the cell and electrodes are carefully freed from oxygen, (a) the electrode potential is a linear function of the surface concentration of hydrogen and (b) the current density i , which will be a measure of the quantity $(-\partial\Gamma/\partial t)$, of electromotively active hydrogen removed from the electrode per unit accessible area, varies logarithmically, over a wide range of current densities, with the observed electrode

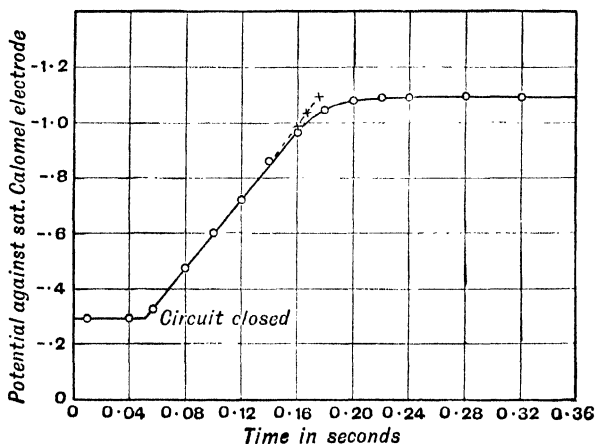


FIG. 90.—ESTABLISHMENT OF THE HYDROGEN OVER-POTENTIAL.

potential E of the metals investigated. Moreover, there is a maximum reversible current i for each metal, below which there is no further decrease in cathode potential. The over-potential η is therefore given by

$$\eta = b(\log i - \log i_0)$$

or

$$\eta = a + B \log i$$

where $a = -b \log i_0$. This relation between over-potential and current density is the same as that put forward by Tafel.

The changes in potential prior to the establishment of the hydrogen over-voltage, in which the potential shows first a linear variation with time but falls off in the vicinity of its over-voltage until the rate of discharge of hydrogen ions is equal to the current, are represented in Fig. 90 for the

mercury electrode.¹ During the initial stages, where the slope is constant, the whole flow of electricity is increasing the charge on the double layer, and there is no appreciable transport of electricity across it. The slope of the curve therefore measures the increase in charge per unit increase of potential $\partial q/\partial t$ —i.e., the capacity C of the double layer. Thus

$$C = \frac{\partial q}{\partial v} = \frac{i \partial t_2}{\partial v} \quad . \quad . \quad . \quad (490)$$

This method therefore allows determinations to be made of the real areas of electrodes of solid metals.³

The actual mechanism by which the hydrogen is liberated is also suggested by these measurements, for the general magnitude of the adsorbed layers, which appear at most to be of molecular dimensions, is best explained by assuming that the electrode potential is due to the presence at the surface of electric doublets formed by the reorientation by distortion of the adsorbed gas. The potential across the interface will then be controlled by the number and magnitude of these dipoles. The process of the liberation of hydrogen and oxygen should therefore have exactly the same kinetics as an ordinary surface reaction in which only those dipoles possessing more than a certain minimum activation energy can leave the surface and form free gas molecules. The value of this energy will obviously depend both on the temperature and on the electrical potential across the double layer, and assuming it to be proportional to v , the potential difference, it will be given by

$$W = \alpha_H v + w_H \quad . \quad . \quad . \quad (491)$$

for the case of hydrogen, w_H and α_H being constants. Hence the number N , of dipoles which can escape will be

$$N = N_0 \exp. \left(- \frac{\alpha_H v + w_H}{RT} \right) \quad . \quad . \quad (492)$$

¹ Bowden and Rideal, *loc. cit.*

² Compare the measurements of Frumkin and Proskauer (*Trans. Faraday Soc.*, 31 (1935), 110) of the capacity and thickness of the double layer.

³ Bowden and Rideal, *Proc. Roy. Soc.*, 120 (1929), 80.

$$\text{and hence} \quad \ln N = \ln N_0 - \frac{\alpha_H v + w_H}{RT} \quad (493)$$

$$\text{or differentiating (493)} \quad \frac{\partial \ln N}{\partial \psi} = \frac{\partial \ln i}{\partial \psi} = \frac{w_H + \alpha_H v}{RT^2} \quad (494)$$

The fact that equation (494) has been fully verified with considerable accuracy for both oxygen and hydrogen on a number of metallic electrodes, lends strong support to the view of the mechanism by which these gases are liberated, which has been put forward by Bowden.¹

In the case of the establishment of the oxygen over-potential at platinum electrodes it appears from the change in potential prior to the actual establishment of the over-potential, that a quantity of electricity is required which corresponds with that required to liberate a monomolecular layer of oxygen adsorbed at the surface. Only provided this layer is not destroyed will the quantities of electricity required to change the potential correspond to the capacity of the double layer formed at the electrode.²

The rate of decay of the over-potential when there is no transfer of electric charges across the double layer, will be given by

$$C \frac{\partial v}{\partial t} = i \quad (495)$$

but, when electric charges cross the double layer at a rate i' representing a depolarisation current, the rate of change of potential will be :³

$$C \frac{\partial v}{\partial t} = i - i' \quad (496)$$

Since only the value of $i - i'$ can change the charge of the double layer it follows that $i = i'$ at the constant over-potential. If now the current is stopped—i.e., if the over-potential is allowed to decay, the rate of change of potential should be obtained by putting $i = 0$ —i.e., from (496)

$$C \frac{\partial v}{\partial t} = -i' \quad (497)$$

¹ F. P. Bowden, *Proc. Roy. Soc.*, **126** (1929-30), 107.

² Butler, Armstrong, and Himsworth, *ibid.*, **137** (1932), 604; **143** (1933), 89.

³ Butler and Armstrong, *ibid.*, **137** (1932), 604.

Tafel's equation (489) gives the rate at which the current continues to be transferred from the metal to the solution in terms of the potential V as

$$i' = Ke^{aV} \quad . \quad . \quad . \quad (498)$$

$$\text{i.e.,} \quad -\frac{K}{C}e^{aV} = \frac{\partial v}{\partial t} \quad . \quad . \quad . \quad (499)$$

$$\text{or} \quad e^{aV_t} - e^{aV_0} = \frac{\alpha Kt}{C} \quad . \quad . \quad . \quad (500)$$

V_t being the potential when the decay has been allowed to continue for a time t , and V_0 that at the moment when the current was stopped. This relationship has been verified experimentally from measurements of the rate of decay of the hydrogen over-potential at a mercury surface.¹ Now, it has been assumed in the above analysis that, after the current has been stopped, the electrons are transferred from metal to solution in accordance with Tafel's equation. If, however, any electromotively active material were formed as a result of the electrolysis, it would yield electrons to the metal, and the depolarisation current would therefore not be as great as that assumed in the calculation. In this particular case at least, therefore, of a metal having a high over-voltage, the products of electrolysis cannot be electromotively active, and similar results have been observed in the case of oxygen on platinum.²

The Quantum Mechanical Interpretation of Over-voltage.

Any theory which attempts to explain the over-voltage required for the liberation of hydrogen or oxygen from different metals must be able to account for the Tafel equation (489)

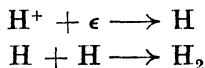
$$i = Ke^{-aV}$$

since all the best experimental evidence shows that this relation is obeyed when complicating factors are excluded. It is also established, from the experiments of Bowden and

¹ Armstrong and Butler, *Trans. Faraday Soc.*, **29** (1933), 1261.

² Butler and Drewier, *ibid.*, **32** (1936), 427.

Rideal, that the over-voltage is associated with the first of the two processes



which are the two possible rate controlling factors.¹ The undischarged ions produced by the electron process then form a double layer. On this basis Gurney has put forward a theory, using the principles of quantum mechanics, which explains the conditions necessary to bring about this discharge of hydrogen ions and which gives the Tafel equation when it is worked out quantitatively.² According to quantum mechanics, neutralisation of an ion does not necessarily involve impact.³ The state of a metal, constituting in this case an electrode, may be characterised by a work function ϕ which is equal to the negative energy of the highest occupied electron level in the metal. In solution the ions will be hydrated (see Chapter XI), and therefore the energy E evolved when one of these is neutralised will not be equal to the ionisation potential I , but will be less than this by a quantity W equal to the heat of hydration of the ion. The relative magnitudes of the work functions of the ion and of the metal will then determine whether or not an electron transition is possible, for such a transition can only take place when there is a vacant level in the metal associated with the same energy as one in the neighbouring ion. From the potential diagram it is therefore clear that, in the case of a positive ion the condition for transition is

$$E_+ = I_+ - W_+ > \phi \quad . \quad . \quad (501)$$

and for the neutralisation of a negative ion

$$E_- = I_- + W_- < \phi \quad . \quad . \quad (502)$$

¹ See for example, Erdey, Grúz, and Volmer, *Z. physikal. Chem.* (A), **150** (1930), 203.

² R. W. Gurney, *Proc. Roy. Soc.*, **134** (1931), 137; *Trans. Faraday Soc.*, **28** (1932), 447. Cf. also the earlier theory of Horiuti and Polanyi *Acta Phys. Chem. U.S.S.R.*, **2** (1935), 505, which suggests that the primary process consists of the transfer of hydrogen ions to adsorption positions at the surface of the metal in the course of which neutralisation occurs—under the assumptions made, this process has a high activation energy.

³ Oliphant and Moon, *Proc. Roy. Soc.*, **127** (1930), 388.

If, now, these conditions are not fulfilled, the influence of the electrode potential may be such as to enable neutralisation to take place, and therefore a current to pass, by building up

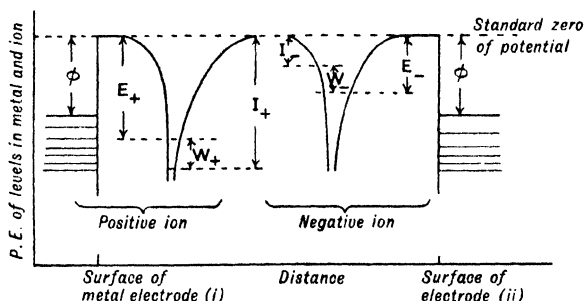


FIG. 91.—CONDITIONS FOR NEUTRALISATION OF (a) A POSITIVE ION, (b) A NEGATIVE ION.

the levels in the metal. Thus in the case illustrated in Fig. 92, where transitions are not possible, a current could pass only if the levels in the metal were raised by the increase in the negative or cathodic potential of the metal until the

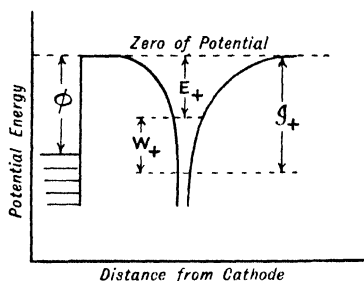


FIG. 92.—CASE WHERE TRANSITIONS ARE NOT POSSIBLE.

work function of the metal was less than E_+ . If V denotes this potential, the condition for a current to flow will be, for positive ions,

$$\phi - eV_c < E_+ \quad . \quad . \quad . \quad (503)$$

or for negative ions,

$$\phi + eV_a > E_- \quad . \quad . \quad . \quad (504)$$

The theory is complicated, however, by the fact that not all the levels below ϕ in the metal are occupied, nor are all the

levels above it unoccupied, nor is the hydration energy W_+ a definite quantity, but is distributed according to the Boltzmann law among a series of energy levels in the ion. When allowance is made for these factors, a probability can be calculated for the transition of the electrons across the potential barrier between the metal and the adjacent ion in the solution. When the expression so obtained is integrated to give the current density, it is necessary to assume that the limits of integration represent only a small

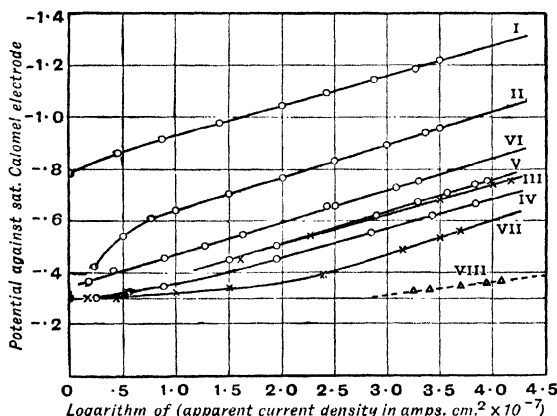


FIG. 93.—EXPERIMENTAL VERIFICATION OF THE TAFEL RELATIONSHIP.

- I. Mercury.
 II, III. Platinised silver.
 IV, V. Etched silver.
 VI. Polished silver.
 VII. Bright platinum.
 VIII. Spongy platinum (current density in amps. $\times 10^{-6}$).

range of potentials in order to simplify the result. The value obtained for the current density at the cathode is then of the form

$$\log i = \frac{E_0 - E_1 + eV}{\gamma kT} + \log T + \text{constant} \quad (505)$$

$$\text{or} \quad i = K \exp. \left(\frac{E_0 - E_1 + eV}{\gamma kT} \right) \quad (506)$$

where E_0 and $E_1 + eV$ are the limits of potential over which the integration is performed, and γ is, to a first approximation, constant. Equation (506) which may be written

$$i = K e^{-\alpha e} \quad (507)$$

is exactly identical with that found empirically by Tafel, and if γ is given the not improbable value of 2, it agrees excellently with the best experimental results of Bowden, the observed and experimental values of the constant A (see below) being in each case $1.7 \times 10^{+6}$. By differentiating the above expression with respect to voltage we have :

$$\frac{\partial \log i}{\partial v} = \frac{A}{T} \quad . \quad . \quad . \quad (508)$$

This result is expressed more familiarly by stating that $\log i$ varies directly with the over-voltage at a given temperature. Fig. 93 illustrates well the manner in which Bowden and Rideal's work has confirmed this for a number of metals showing different hydrogen over-potentials. One further relation which is predicted by Gurney's theory, and which has been completely confirmed by experiment is the variation of the current density with the temperature, obtained by differentiating equation (505) with respect to temperature,

$$\frac{\partial \log i}{\partial T} = \frac{E_1 - E_0 - eV}{\gamma k T^2} + \frac{1}{T} \quad . \quad . \quad (509)$$

$$\text{or} \quad \frac{\partial \log i}{\partial T} = \frac{B}{t} \quad . \quad . \quad . \quad . \quad . \quad . \quad (510)$$

where B is a function varying with the potential V . By giving to the range of potentials E_0 to $E_1 - eV$ (which corresponds to the overlap of the energy levels over which the probability is integrated) the value of one electron volt, and preserving the value of $\gamma = 2$, the calculated value of B at 320° A. is 0.057, again agreeing well with the observed values of 0.05 to 0.06 between 227° A and 353° A.¹

Kinetic Considerations in the Establishment of Over-voltage.

It has already been mentioned (see footnote, p. 335) that an adsorption theory of over-voltage has been put forward to account for the observed effects,² and Butler³ supposes that both mechanisms—viz., the formation of atomic

¹ Bowden, *loc. cit.*

² Horiuti and Polanyi, *Acta Phys. Chem. U.S.S.R.*, **2** (1935), 505.

³ J. A. V. Butler, *Proc. Roy. Soc.*, **157** (1936), 423.

hydrogen accounted for in Gurney's theory and the formation of adsorbed hydrogen atoms—can play a part in the general case of over-voltage, but that Gurney's theory only gives a complete account of the experimental effects in the case of metals of high over-voltage. The energy of a hydrogen atom in the region between the metal and adjacent water molecules may be obtained by combining the energy of adsorption A with the repulsive energy R between the atom and the water. AA is the joint curve so obtained, and by comparison with Gurney's function (BB), $I - W$, the energy of activation of the process of adsorption

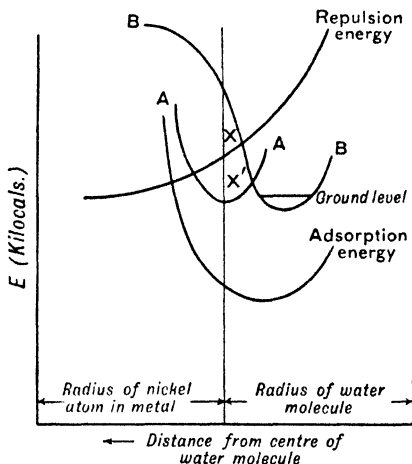


FIG. 94.—ENERGY DIAGRAM IN NEIGHBOURHOOD OF AN INTERFACE (Butler).

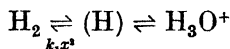
is equal to the difference between the energy at the point of intersection X' and that of the proton in the ground state. This activation energy is therefore considerably less than that for the process of formation of free atomic hydrogen, which will be denoted by the energy difference between the ground level and the intersection X .

With metals capable of adsorbing hydrogen in the atomic condition, the energy of adsorption is of the same order (by calculation) as $D/2$, where D is the dissociation energy of the hydrogen molecule—i.e., $A \simeq 2e$ volts and DV is of the order 1 volt. It therefore appears that adsorbed

hydrogen may be formed at a much less negative voltage than is required for the production of free hydrogen by Gurney's mechanism.

This process is reversible, and the reversible hydrogen potential is that at which the transfers occur at the same rate in both directions—*i.e.*, at such a potential that the energy of activation is the same from either side. Calculation shows that this mechanism leads to small values for the activation energy of the reversible transfer, the more probable configuration having an activation energy of about 8 kilocalories. At such an electrode, the passage of currents of the order 10^{-5} amps./cm.² would not greatly disturb the equilibrium potential.

At the reversible hydrogen electrode adsorbed hydrogen must be in reversible equilibrium with the atmosphere of hydrogen—*i.e.*.



and if x be the number of adsorbed positions on the surface

$$\left. \begin{array}{l} \text{Rate of desorption} = k_1 x^2 \\ \text{Rate of adsorption (depending on finding two} \\ \text{adjacent vacancies)} = k_1'(1 - x)^2 p_{\text{H}_2} \end{array} \right\} \quad (511)$$

i.e., at equilibrium

$$k_1(x)^2 = k_1'(1 - x)^2 p_{\text{H}_2} \quad . \quad . \quad . \quad (512)$$

When hydrogen is being liberated, this condition is disturbed and the rate of formation of hydrogen molecules is :

$$i = k_2 x^2 - k_1' p_{\text{H}_2} (1 - x)^2 \quad . \quad . \quad . \quad (513)$$

Thus the rate of production of hydrogen in this way cannot exceed k_1 .

For the other equilibrium, from the solution to the surface, if the rate of transfer of protons at the equilibrium potential difference V_0 to a completely unoccupied surface, is k_0 and if the rate of transfer in the opposite direction from a completely occupied surface is k_0' , then for equilibrium

$$k_0' x = k_0 (1 - x) \quad . \quad . \quad . \quad (514)$$

at V_0 . When the potential is displaced by ΔU , the rates therefore become

$$k_0(1 - x) \exp. \left(\frac{-e \cdot \Delta V}{\gamma kT} \right) \text{ and } k_0'x \exp. \left(\frac{e \cdot \Delta V}{\gamma kT} \right)$$

and the current is now :

$$i = k_0(1 - x) \exp. \left(\frac{-e \cdot \Delta V}{\gamma kT} \right) - k_0'x \exp. \left(\frac{e \cdot \Delta V}{\gamma kT} \right) \quad (515)$$

There are three special cases for which this general equation may be simplified.

(1) when i is small compared with k_1 the adsorption is not appreciably disturbed by the passage of a current, so that if

$$i_0 = k_0(1 - x) \quad \text{. . . .} \quad (516)$$

$$\text{then} \quad \frac{i}{i_0} = -2 \left(\frac{e \cdot \Delta V}{\gamma kT} \right) \quad \text{. . . .} \quad (517)$$

i.e., for small displacements in V the change in potential is proportional to the current, as is found to be the case for reversible electrodes.

(2) As $i \rightarrow k_1$, $(1 - x) \rightarrow 0$ and ΔV increases more rapidly than in (1).

(3) When $i > k_1$ the mechanism is no longer capable of accounting for the whole of the current, and the potential of the electrode must rise until some other discharge process such as that postulated by Gurney becomes possible.

Thus the behaviour of an electrode is, according to Butler, determined by the value of V , which in turn depends on the activation energy of desorption of hydrogen from the metals. There appears, in fact, to be an optimum spacing for each metal in order that adsorption of hydrogen shall occur, and the fact that brightly polished platinum surfaces will only give the reversible hydrogen potentials with difficulty, may be attributed to the unsuitable spacings present, possibly arising from the existence of a "Beilby layer" at the surface of the polished metal. In the case of platinum black, however, there is a greater probability of finding suitable spacings on the surface, both because the metal is unpolished, and due to its much greater superficial

area, and it is therefore possible for the reversible hydrogen potentials to be observed in contact with such an electrode. The formation of adsorbed hydrogen below the normal over-voltage has never been actually demonstrated, but, due to the sensitiveness of the process to the presence of traces of oxygen, the measurements always have to be carried out in the presence of hydrogen, and it is doubtful whether any indication of its independent formation could be found.

CHAPTER XI

IONS IN SOLUTION

IN the simplified electrostatic model which Debye and Hückel used in their theory, the ions were assumed to be point charges and, to a first approximation, the dielectric properties of the solvent were supposed to be unaltered by the presence of the ions. A little consideration shows us at once, however, that such an assumption cannot be made, even in the most dilute solutions. The water molecule has been shown to have a triangular structure with the oxygen atom at the apex of the triangle. From measurements on the *X*-ray scattering¹ and by wave mechanical calculations,² the angle in the case of water appears to be between 90° and 120° and the moment of the molecule is 1.85×10^{-18} e.s.u. If the ordinary Coulomb law of attraction is assumed to hold at molecular distances, we may make a rough calculation of the intensity of the field at a distance of, say, 10 Å. from a singly charged ion. For

$$\frac{e}{r^2} = \frac{4.77 \times 10^{-10}}{10^{-14}} = 4.77 \times 10^4 \text{ e.s.u.} \quad . \quad . \quad (518)$$

Since one e.s.u. is equal to 300 volts, the field due to such an ion will have an intensity of about 14×10^7 volts per cm. The orienting force on the dipole molecules of the solvent will therefore be enormous at close distances, and the small deorientation due to thermal agitation will be quite insignificant. We are led therefore to suppose that ions in solution must be in a different condition from those in a gas, but the exact nature of this difference is still one of the major unsolved problems of electrochemistry.

¹ Debye, *Physikal. Z.*, **31** (1930), 142, 419.
Z. Electrochem., **36** (1930), 612.

² Pauling, *J. Amer. Chem. Soc.*, **53** (1931), 1367.

A simple electrostatic picture gives some idea of the nature of solvation without any detail as to its mechanism. A sodium ion moving through partially dried hydrogen has been shown to take up one water molecule, giving a polyatomic ion $(\text{Na} \cdot \text{H}_2\text{O})^+$.¹ Such an ion has a potential energy curve exactly like a diatomic molecule in which the attraction between the components changes over at the distance corresponding with the minimum potential energy, into a repulsive force which increases indefinitely as the distance

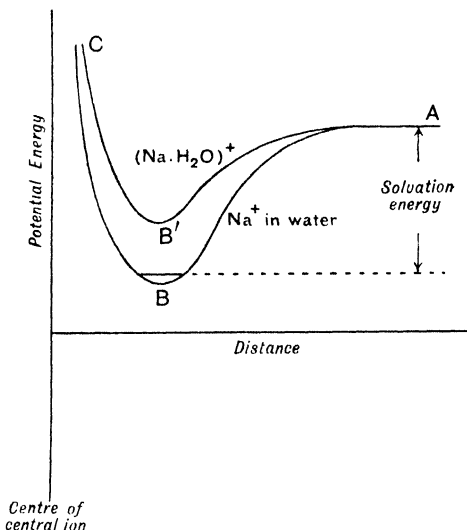


FIG. 95.—POTENTIAL ENERGY CURVES FOR IONS IN SOLUTION.

is further decreased. This can easily be understood when we remember that the water molecule has the same number of electrons as the neon atom. An ion $(\text{Na} \cdot \text{H}_2\text{O})^+$ will therefore presumably consist of closed electronic shells which give it a behaviour exactly like a diatomic molecule, while the complex retains the properties of the sodium atom. If now several water molecules are brought simultaneously within the field of a Na^+ ion, the potential energy curve will be modified only by the deepening of the trough (Fig. 95), and this deepening will tend to a limit as more and more solvent molecules are brought near the ion. This limit

¹ Powell and Brata, *Proc. Roy. Soc., A*, 138 (1932), 129.

will therefore correspond to the ion being entirely surrounded by solvent and the depth of the potential energy trough from A (the P.E. for the Na^+ ion in its ground state) to the lowest level will therefore be the solvation energy of the ion. This solvation energy may be calculated (see p. 350) from the ordinary laws of electrostatics if the central ion is regarded as a spherical conductor with the charge of the ion uniformly distributed over its surface and the solvent is considered as a uniform dielectric.¹

From this simple treatment, it would appear, therefore, that an electrolyte ion has all the properties of a polyatomic ion in which the solvation energy is substituted for the dissociation energy. Only when a solution is dilute, however, will it be possible on the above reasoning to think of the solvent as consisting largely of unaffected solvent molecules with a few solvated ions moving within it. At higher concentrations, the volume of unaffected solvent is very small compared with the total volume of the solution, and all the properties of the solution will therefore be affected.²

This method of determining the state of an ion in solution has, however, ignored the essentially discontinuous character of the solvent medium. For, although it has assumed that the solvent molecules are brought up individually to the central ion, there is no consideration given to the size of the solvent molecules compared with the size of the central ion. The water molecule always has a radius of the same order as that of the central ion (*e.g.*, the radius of Na^+ is $0.98 \text{ \AA}$., while the radius of the water molecule is of the order $1 \text{ \AA}$.), and we know that if the solvent molecules are brought too close to the central ion, there is a repulsive force, and not an attractive force between them. As soon, therefore, as the first solvent molecules have become attached to the central ion, there is a shielding effect against the attraction of further solvent molecules by the central ion, and the magnitude of this effect depends upon the size of the central ion, upon its charge

¹ R. W. Gurney, "Ions in Solutions" (Cambridge, 1937), Chap. I, p. 1.

² *Idem*, *loc. cit.*, pp. 21-24.

and on the size and magnitude of the dipoles of the solvent molecules. The shielding effect will not, however, prevent other solvent molecules being attracted to the first group by virtue of their mutual dipole forces, but whereas the first sheath will be firmly attached to the central ion, the subsequently attracted solvent molecules will come much more under the influence of thermal agitation and any particular molecule in this secondary sheath will be only in temporary union with the central ion. We must therefore conclude that an ion in solution may, in general, have an effective radius greater than that of the ion in the gaseous state.

Experimental Evidence for the Solvation of Ions in Solution.

A considerable amount of experimental work has been carried out in the belief that the radius of a solvated ion could be determined, and much of the evidence serves, at least, to demonstrate the necessity, on experimental grounds alone, of regarding an ion in solution as solvated. The limiting mobilities of the alkali metal ions in water, for example, show that there is a gradual rise in the value of this property from the smallest to the largest ion, whereas, from the sizes of the ions determined in their solid compounds, the reverse order of velocities would be expected if the ions were unchanged in solution. The mobilities and lattice sizes of some common ions in water at 25° C. are given in Table IX, and these illustrate the anomaly very well.

A similar order for the ionic mobilities is observed in other solvents. Bredig¹ first suggested that these anomalous mobilities might be due to the formation of hydrates of the alkali metal ions, the lithium ion being the most heavily hydrated, and therefore the largest. These hydrated ions were supposed to be able to migrate as a whole under the influence of an applied potential difference. On the basis of this theory, Born² has deduced an expression for the mobilities of ions in terms of their radii, but the values obtained for the radii of the halogen and alkali metal ions are

¹ Bredig, *Z. physikal. Chem.*, **13** (1894), 277.

² M. Born, *Z. Physik.*, **1** (1920), 221.

all less than 10^{-8} cm.—*i.e.*, less than the values which they have in the crystals of alkali halides. A simple qualitative extension of Bredig's view may, however, be given as follows. Around an ion in solution, there is a powerful electric field, which, for a given charge on the ion, is more intense the smaller the (unsolvated) ion—*e.g.*, it is more powerful for Li^+ than for Rb^+ . The modification in the electrostatic field of the water dipoles produced by their attraction into a semi-permanent agglomeration round the ions in solution,

TABLE IX.

Limiting Ion Mobilities and Crystal Ion Radii of Some Ions.

Ion.	Limiting ion mobility.	Crystal ion radius.
H^+	349.72 ¹	1.36 Å. ²
Li^+	38.68 ¹	0.68 Å. ²
Na^+	50.10 ¹	0.98 Å. ²
K^+	75.50 ¹	1.33 Å. ²
Rb^+	78.43 ³	1.48 Å. ²
Cs^+	79.91 ³	1.67 Å. ²

will be approximately proportional to the polarising power of the ion introduced—*i.e.*, to the ratio charge/radius.⁴ The mobilities of large ions of a given charge—*e.g.*, K^+ , Rb^+ , and Cs^+ in aqueous solutions should therefore be approximately constant, but they should differ greatly from the mobility of a small ion like Li^+ , as borne out by the results shown in Table IX.

The mobilities of ions in unmeasured solvents have been calculated in certain cases by Walden⁵ using an extension of Stokes' law, which was assumed for this purpose to apply

¹ D. A. MacInnes, T. Shedlovsky, and L. G. Longworth, *J. Amer. Chem. Soc.*, **54** (1932), 2758.

² Zachariasen, *Z. Krist.*, **80** (1931), 137.

³ R. T. Lattey, *Phil. Mag.*, **6** (vii) (1928), 258.

⁴ The radius in this expression is that of the unsolvated ion as found from measurements of crystal dimensions.

⁵ Review by H. Ulich, "Über die Beweglichkeit der electrolytischen Ionen," *Fortschritte der Chemie*, (1926), 569.

to ions in solution.¹ It follows immediately from the equation

$$F = \text{friction force} = 6\pi\eta rv \quad . \quad . \quad (519)$$

where η is the viscosity of the medium and v and r are the velocity and radius, respectively, of the moving particle, that the velocity is inversely proportional both to the viscosity and the radius—i.e., for a constant radius and at a constant temperature

$$\begin{array}{l} \text{velocity} \times \text{viscosity} = \text{constant} \\ \text{or} \quad \Lambda_{\infty}\eta = \text{constant} \quad . \quad . \quad . \quad (520) \end{array}$$

This equation (Walden's rule) has been found only to apply with any degree of accuracy to large ions occurring in what Walden classes as "normal" electrolytes² (mostly organic derivatives of NH_4^+). It has been used to evaluate the mobilities, in new solvents, of such ions—e.g., $\text{N}(\text{CH}_3)_4^+$ —from measurements of the conductivity of a salt of the ion in the solvent—e.g., for the iodide (520) becomes,

$$\eta\Lambda_{\infty(\text{NMe}_4)\text{I}} = \eta\lambda_{\infty\text{I}^-} + \eta\lambda_{\infty\text{NMe}_4^+} \quad . \quad . \quad (521)$$

The large symmetrical tetralkylammonium ions are found to have a higher mobility in a given solvent than the ammonium ion, which is itself much smaller, a fact which suggests that the smaller NH_4^+ has a much higher number of attendant water molecules. Walden has therefore used the variations of the product of the mobility of an ion and the viscosity of the solvent, in a number of solvents as a measure of the extent to which the ionic radius changes in the different solvents.

Walden's equation is, however, not in agreement with experimental evidence obtained from a study of transport

¹ Whether Stokes' law is applicable to ions in solution is a question which cannot be answered at present from theoretical considerations. But the fact that the product $\Lambda_{\infty}\eta$ is almost constant with temperature in very many non-aqueous solutions, and in some aqueous solutions also, seems to justify *a posteriori* the application of Stokes' law to ions in these cases at least: see H. Ulich, *Trans. Faraday Soc.*, **23** (1927), 414.

² P. Walden, *Z. physikal. Chem.*, **147** (1930), 1; **55** (1906), 207. "Salts, Acids, Bases," New York, 1929. There is some discrepancy among the results of various workers as to whether Walden's rule holds even for "normal" electrolytes.

numbers in mixtures of light and heavy water.¹ From equation (104) the limiting transport number should be independent, according to Walden's equation, of the solvent. This is not observed experimentally (see p. 130).

A further objection to the application of equation (520)

$$A_{\infty}\eta = \text{constant}$$

to aqueous solutions of a particular compound and its ions arises from quite different considerations. It is known that water possesses a definite crystalline structure with which is associated its bulk viscosity, and that in the neighbourhood of an ion this structure is broken down.² The viscosity of the medium around an ion is therefore very different from the bulk viscosity. There is evidence that similar recurrent crystalline patterns as that on which water is built up, may also occur in other solvents,³ and for a particular electrolyte and its ions the viscosity of the medium in Walden's equation in the immediate vicinity of any ion would be indeterminate, and the rule could not be applied with accuracy. Furthermore, any attempts to determine the relative degrees of ionic hydration from an application of Stokes' law will give a measure of the amount of water carried hydrodynamically through the liquid by the motion of the ion. This will always be higher than the amount associated with the ion at rest.

There are, however, many other physical properties of electrolytic solutions which give evidence of the existence of solvent sheaths round ions in solution.⁴ The densities of ionic solutions allow estimates to be made of the relative volume contributions of the individual ions in solution for, in very dilute solutions, the volume alterations per ion pair are additive and approximately proportional to the ionic sizes. Except in the case of the larger ions like Cs^+ , these are not the same as the apparent volume contributions

¹ J. C. Chittum and V. K. La Mer, *J. Amer. Chem. Soc.*, **59** (1937), 2425.

² J. Bernal and Fowler, *J. Chem. Physics*, **1** (1933), 515.

³ J. A. Prins, *Z. Physik.*, **56** (1929), 617.

⁴ For a review of evidence for ionic hydration see N. Dhar, *Z. Electrochem.*, **20** (1914), 57.

Fricke, *ibid.*, **28** (1922), 111.

calculated from the volume of the ion in the solid state, the difference being due to the sheath of hydrated water molecules round the ion.¹ Again, it should be possible to observe a difference between the actual masses of anions and cations in solution from measurements in electrolytes under supersonic vibrations. Normally the dynamical reactions of the masses under the influence of an alternating field are negligible compared with viscous forces, but when the frequency becomes extremely high, as with supersonics, their effect should be appreciable. Moreover, due to the different movement of the two types of ions present, which normally have different masses, a separation of the positive and negative charges should take place giving rise to a periodic potential difference in the electrolyte, of the same frequency as that of the applied vibrations. Debye has calculated the maximum magnitude of the potential difference in this potential wave to be of the order 10^{-6} volt in a uniunivalent electrolyte at a concentration $N/1000$ ² but although a more exact theory of the effect has been developed to allow for the relaxation and electrophoretic forces present,³ no measurements have yet been made. The method would allow an approximate estimate of the effective ion masses in very dilute solutions, to be made.

The Heat of Solvation and "Effective Ionic Radius."

It is quite evident, from what has been said in the previous section, that ions in solution do not exist in the same state as in gases or crystals. In transferring an ion from the gaseous or crystal state, to a solvent, there will therefore in general be a definite heat of solvation, depending on the nature of the ion and the differences produced in the configuration of the solvent by the presence of the ion. We shall be concerned only with aqueous solutions. For gaseous ions the heats of hydration have been estimated by applying Born's cycle to the determination of the lattice energy U of a salt,⁴ which gives the energy required to

¹ Bernal and Fowler, *loc. cit.*

² P. Debye, *J. Chem. Physics*, **1** (1933), 13.

³ S. Oka, *Proc. Math. Phys. Soc. Japan*, **15** (1933), 415.

⁴ M. Born, *Verh. der Deutsch. Phys. Gesellschaft*, **21** (1919), 13, 679.

convert the salt into gaseous ions, and by supposing that when these are dissolved in water, an amount of energy is liberated, equal to the sum of the heats of hydration of the anion and cation. Thus

$$(F_{\text{H}})_{\text{anion}} + (F_{\text{H}})_{\text{cation}} = Q_{\text{solution}} + U \quad . \quad . \quad (521)$$

where Q_{solution} is the heat of solution. Calculations made in this way show that almost all the work necessary to break up the crystal is furnished by the heat of hydration. Fajans supposed, in fact, that the heats of hydration of gaseous ions constituted a quantitative measure of the action of the ions on the solvent dipoles,¹ and the theory has been extended by Born² and Schmick³ to give approximate values for the ionic radii in solution and the degrees of hydration in certain cases. Exception may be taken to the term "degree of hydration" as implying the association of a stoichiometric quantity of water with an ion. It is, however, quite logical to use an "effective ionic radius" in solution provided this is not associated with a definite ionic model (see p. 354).

From simple electrostatic considerations, it is possible to calculate the value of this ionic radius r_i in terms of the heat of hydration, provided the discontinuous structure of water is replaced by a continuous electrically polarisable medium. Assuming, for a first consideration, that the dielectric constant D of the medium is constant, and that the charge on the ion is ze , then its energy in a field of strength E is given by

$$U = \frac{1}{8\pi D} \int E^2 ds \quad . \quad . \quad . \quad (522)$$

¹ Fajans, *Verh. D. Phys. Ges.*, **21** (1919), 549, 709.

Latimer (*J. Amer. Chem. Soc.*, **48** (1926), 1234) has assumed that there is an approximate proportionality between the entropy of a solution and the heat of solution of gaseous ions. By defining a standard state arbitrarily, values are found for the entropies of aqueous ions. See Latimer and Buffington, *J. Amer. Chem. Soc.*, **48** (1926), 2297; Latimer and Kasper, *ibid.*, **51** (1929), 2293; Latimer, Schutz, and Hicks, *J. Physical Chem.*, **3** (1934), 82; Latimer, *Chem. Rev.*, **18** (1936), 349.

² M. Born, *Z. Physik.*, **1** (1920), 45.

³ H. Schmick, *ibid.*, **24** (1924), 56.

where the integration is carried out over the whole surface. The value of E is

$$E = \frac{ze}{r^2} \quad . \quad . \quad . \quad . \quad (523)$$

and transferring to polars,

$$dS = r^2 dr d\omega \quad . \quad . \quad . \quad . \quad (524)$$

where $d\omega$ is an element of solid angle. By substitution into (522) we have :

$$U = \frac{1}{8\pi D} \int_0^{4\pi} d\omega \int_{r_i}^{\infty} \frac{z^2 e^2}{r^4} r^2 dr = \frac{z^2 e^2}{2Dr_i} \quad . \quad . \quad (525)$$

Hence the electrostatic energy of an ion in a vacuum is :

$$\frac{z^2 e^2}{2r_i} \quad . \quad . \quad . \quad . \quad (526)$$

and in water (dielectric constant D_w) it is

$$\frac{z^2 e^2}{2D_w r_i} \quad . \quad . \quad . \quad . \quad (527)$$

The difference between the expressions (526) and (527) will represent the work done in bringing the ion from the gaseous state into water and by multiplying by Avogadro's number N and the heat equivalent of the erg, 2.388×10^{-11} kg.-cals. the heat of hydration F_H is obtained as :

$$F_H = \frac{1}{2} \left(1 - \frac{1}{D_w} \right) N \times 2.388 \times 10^{-11} \cdot \frac{e^2 z^2}{r_i} \text{ kg.-cals.} \quad (528)$$

Substituting $D_w = 81$; $N = 6.06 \times 10^{23}$ and $e = 4.774 \times 10^{-10}$, (528) becomes

$$F_H = 1.64 \times 10^{-6} \cdot \frac{z^2}{r_i} \text{ kg.-cals.} \quad . \quad . \quad (529)$$

For hydrogen, using the value $F_H = 262$ determined by Fajans, $r_i \times 10^8 = 0.625$.

This method of calculating the heat of hydration in terms of the ionic radius is, however, certainly incorrect,¹ for it has assumed that the dielectric constant of the solvent is constant near an ion, that the radius effective for the above calculation is the true ionic radius, and that there is no expenditure of

¹ T. J. Webb, *Proc. Nat. Acad. Sci. (Baltimore)*, **12** (1926), 524.

work due to compression of the solvent near an ion. A more exact calculation has been made by a method which does not assume a constancy of the dielectric constant of the medium.¹ The radius r_0 used is that of a cavity surrounding each ion, in which there are no solvent molecules. The electrical work W done in charging an ion in the molecular medium and the compression work W_r , which is expended in compressing the solvent due to the attraction of its dipolar molecules near an ion, may both be computed graphically for any particular value of the radius r_0 . In a vacuum (526) gives the value of the energy of the electric field exterior to the cavity of radius r_0 , so that, denoting by F_H , the free energy of hydration of the ions, we have :

$$F_H = \frac{z^2 e^2}{2r_0} - (W + W_r) \quad . \quad . \quad . \quad (530)$$

Since all the quantities on the right-hand side of (530) are functions of r_0 , we may write :

$$F_H = f(r_0) \quad . \quad . \quad . \quad (531)$$

Also the electrical energy of charging the ion in the solvent will from (527) be :

$$W = \frac{e^2 z^2}{2r_0 D'} \quad . \quad . \quad . \quad (532)$$

where D' is the virtual dielectric constant of the medium which will of course depend upon r_0 . Since W has been calculated independently of equation (532), no value is ascribed to D' in calculating F_H .

Since there is no evidence for the absolute values of F_H , another property must be calculated as a function of r_0 if values of this radius are to be computed for any given ion. Now, the partial molar volume of an ion depends upon the effective volume of the ions and on the contraction (electrostriction) of the solvent due to the electric fields of the ions. Both these quantities may be estimated in a particular case, giving the partial molar volume of an ion as a function of its radius. If we now consider two ions A and B for which the sum or difference of the partial molar

¹ T. J. Webb, *J. Amer. Chem. Soc.*, **48** (1926), 2589.

volumes $\bar{V}$ and of the heats of hydration F_H are known, we have from (531) :

$$(F_H)_A + (F_H)_B = f(r_A) + f(r_B) \quad . \quad (533)$$

also $(\bar{V})_A + (\bar{V})_B = \phi(r_A) + \phi(r_B) \quad . \quad (534)$

where the forms of the functions $f(r)$ and $\phi(r)$ have been calculated. It is therefore possible, in the case of any two ions for which there is sufficient experimental evidence, to solve equations (533) and (534) for the effective ionic radii r_A and r_B . In Table X some of the calculated values are given, and it is interesting to note that, both for the alkali metal and for the halogen ions, the order of the effective ionic radii in aqueous solutions is the same as for the radii of the ions in the crystals, although the values are consistently higher in the former case.¹

TABLE X.

Heats of Hydration and Effective Ionic Radii of some Ions.

Ion.	Radius $\times 10^8$.	F_H (K.cals.).	Ion.	Radius $\times 10^8$.	F (K.cals.).
Na ⁺	1.505	99	F ⁻	1.75	87.0
K ⁺	1.873	81.9	Cl ⁻	2.238	70.1
Rb ⁺	2.02	76.9	Br ⁻	2.382	66.2
Cs ⁺	2.19	71.5	I ⁻	2.60	61.0
Zn ⁺⁺	1.04	52.5	H ⁺	<0.5	249.6

The Nature of Solvation.

In the previous discussion we have made no assumptions about the kind of model which may be used to represent ion solvation. A review of the experimental evidence shows that it is possible to obtain some idea of the nature of ion solvation at least in aqueous solutions. It is certain that in the crystalline state, ions, such as the cobalt ion in its hexa- complexes or the metal ions in the vitriols, are hydrated by virtue of their electron acceptor properties which enable them to form co-ordinate covalent links with water

¹ See for example, Bragg, *Proc. Roy. Inst. Gr. Brit.* [iii], 24, No. 119, (1925), 614.

molecules.¹ It seems difficult not to suppose that in solution these same ions may be able to form, with some at least of the associated water sheath, a group of co-ordinated water molecules which will be more permanently attached to the ion than the remaining water molecules. A similar conclusion is reached from a consideration of the potential energy relations near an ion in solution (see p. 343). Evidence in favour of this view has become available from a study of the structure of water. From the results of X-ray diffraction experiments, water appears to have a modified quartz-like structure, which will, however, allow of some close packing. The difference between this modified quartz form and the true tetra-coordinated quartz form is ascribed to the thermal movements of the water molecules, which lead at higher temperatures to a structure approaching the close-packed form more and more closely. Following this view of the structure of water, Bernal and Fowler² have developed a theory of ionic solutions which supposes that, in the neighbourhood of an ion, the water structure is broken down so that the solvent here has abnormal physical properties. There is therefore a critical radius round the ion corresponding with the co-ordination sphere, within which the solvent molecules are no longer held and oriented by their mutual dipole attractions, but are united co-ordinatively with the ion. The number of water molecules which can be accommodated in this permanent fashion around the ion will depend on the steric conditions regulated by the size of the ion, but it is assumed that the water molecules inside the co-ordination sphere are in a permanent state of attachment to the ion, whereas the dipole-associated water molecules outside this sphere may be replaced from the water structure itself at each stage of the ion's progress through the liquid.

This view of hydration as consisting of two phases is supported by the evidence of Fajans from the refractivities of ions in solution and in the crystalline state.³ Precisely

¹ N. V. Sidgwick, "Electronic Theory of Valency," Oxford (1927), Chapter XI.

² Bernal and Fowler, *J. Chem. Phys.*, **1** (1933), 515; *Trans. Faraday Soc.*, **29** (1933), 1049. ³ K. Fajans, *Z. Electrochem.*, **34** (1928), 502.

those ions which, from the considerations outlined above, are hydrated in the permanent sense show values of the refractivities which can only be explained by a lowering of the refractive index of the solvent following the co-ordination of its molecules round the ions.

If the nature of hydration is such that the associated water molecules do form themselves into the co-ordination spheres and the remaining dipole associated molecules remain only loosely attached round an ion, the heat of hydration will consist of four terms due to

(a) The energy of the co-ordination sphere, proportional to the number of water molecules co-ordinated and to the mutual energies of the ions ;

(b) The energy of the dipole associated molecules ;

(c) The energy of the main body of the water where the normal physical properties are observed ;

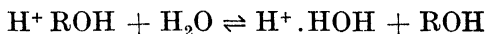
(d) The mutual energy of the water molecules re-oriented from the normal water structure by the dipole forces in the neighbourhood of the ion. This must be subtracted from the expression for the hydration energy.

Unfortunately any estimates of the hydration energy made in this way cannot be compared with expressions observed experimentally, since the Born cycle gives only the sum of the heats of hydration of the ions of opposite charges when the salt is dissolved in water. Without a knowledge of the absolute values of the degree of hydration for a particular ion, this sum of the two separate ionic heats cannot be analysed into its component parts by any method which is independent of theoretical considerations of the nature of the hydration energy.

The Hydrogen Ion in Solution.

The extraordinarily high mobility of the hydrogen ion makes it apparent at once that this ion must have some special relationship to the solvent. It would, however, be impossible for the hydron to be in a different state from that of other ions by existing as a bare proton, for the field

in the neighbourhood of so small an ion would be exceedingly intense, and disturbing effects which are not, in fact, observed would be expected when it came into the fields of other ions. From a long series of experiments on the influence of water on catalysis by the hydrion in non-aqueous solutions, Goldschmidt¹ and Lapworth² independently reached the conclusion that the hydrion could not, in the presence of solvent molecules, be supposed to be an electron-free nucleus, although only Goldschmidt believed that, after the addition of traces of water, the active catalyst was the hydrated hydrogen nucleus. To attribute catalytic properties to the electron-free nucleus would be to affirm that the proton H^+ was unique in having catalytic properties to the degree observed, for it is quite different chemically from any other molecule. No such unique position in the catalytic properties of the hydrion is observed experimentally.³ The hydroxyl ion, for example, is quite as effective a catalyst. Again, the very large diminution in conductivity caused by the addition of traces of water to alcoholic solutions of the halogen acids is quite out of proportion to the alteration in the physical properties of the solvent, and it is attributed to the chemical exchange reaction⁴ (see p. 88):



in which the water molecule has a much stronger affinity for the proton than the alcohol molecule. The importance of this evidence is that it establishes the fact that the free proton exists, if at all, only to a very minute extent in the presence of water or other solvent molecules. The impossibility of the proton existing alone in the presence of other molecules possessing electron systems acting as screens against the surroundings is, according to Fajans, manifested by the enormous heat effect of 232,000 calories produced when the free proton unites with water. A simple

¹ Goldschmidt and Udby, *Z. physikal. Chem.*, **60** (1907), 728.

H. Goldschmidt, *Ber.*, **28** (1895), 3218; *ibid.*, **29** (1891), 2208.

² Lapworth and Fitzgerald, *J.C.S.* (1908), 2163.

³ J. N. Brönsted, *Chem. Rev.*, **5** (1928), 234.

⁴ H. Goldschmidt, *Z. physikal. Chem.* (A), **108** (1926), 121.

calculation shows that, if this heat quantity is supposed to represent the affinity of the proton for water, the concentration of free protons in the solution will be only about 10^{-150} .¹

An X-ray examination of the crystal of perchloric acid monohydrate $\text{HClO}_4 \cdot \text{H}_2\text{O}$ shows that the ions produced in the lattice are H_3O^+ and ClO_4^- .² The unhydrated hydrogen ion H^+ could not be detected directly by such an analysis. It is therefore very probable from the fact that the ion H_3O^+ may occur in the solid state that in aqueous solutions the hydrion is also H_3O^+ . Calculations of the activities of hydrochloric acid in water-alcohol solutions in ideally dilute solutions, where the activity should be proportional to the molecular fraction, give results quite different from those determined on the assumption that there is no association in the chemical sense between solute and solvent. If, however, the hydrogen ion is present as H_3O^+ , not as H^+ , the activity of the water must be considered, and the experimental and theoretical curves then agree over a wide range of mixtures of alcohol and water. The evidence for the nature of the hydrion in aqueous solutions may therefore be summarised as follows: "The assumption of the existence of H_3O^+ fits the experimental data to a better degree of approximation than does the assumption of no chemical action and much better than the postulation of a higher hydrate."³

The knowledge of the structure of water gained from an X-ray examination, and the hypothesis that the hydrion exists in solution as H_3O^+ , together give a possible explanation for the abnormally high mobilities of the hydrion and hydroxyl ion in aqueous solutions. According to the Bernal-Fowler theory of ionic solutions, the hydrion H_3O^+ will, like all other small ions, be more or less hydrated, the extra protons of the H_3O^+ ions being accommodated in the tetrahedral water structure to give an ammonia-like molecule. It would therefore be expected that, unless there

¹ K. Fajans, *Verh. Phys. Gesell.*, **20** (1918), 209.

² Volmer, *Ann.*, **440** (1924), 200.

G. F. Smith and O. E. Goehler, *Ind. Eng. Chem. (Anal.)*, **3** (1931), 58.

³ J. N. Brönsted, *loc. cit.*

were some quite new effect, the mobility of the hydrion would approach that of the ammonium ion which is nearest to it in electronic structure. The fact that it does possess so extraordinarily high a mobility therefore indicates that some quite different process must be taking place. On quantum mechanical grounds it is possible¹ for H_3O^+ to exchange its proton with a water molecule provided the disposition of this is correct for there is, after the exchange, a configuration of equal energy to that in the first state. Since the frequency of these proton jumps depends on the distance through which the proton has to jump, it is possible to calculate from the known structure of water the frequency of the proton transfers, which depends on the frequency with which the correct configurations are presented. This is found to be of the order required to account for the observed mobility.² The abnormal mobility of the hydrion may be attributed, therefore, to a process in which the proton attached to the H_3O^+ ion is handed on very rapidly, due to the favourable configurations of the water molecules with each other, from one water molecule in the structure to the next.

The transfer of the OH^- down the water-chain takes place by the exchange of a hydrogen ion between a water molecule forming part of the chain and the OH^- ion present. This causes a shift in the position of the OH^- ion through a distance equal to that between two neighbouring water molecules. The whole process, which involves the successive transfers of hydrogen ions, makes the extra mobility of the hydroxyl ion above normal ions only about one-half that of the ion H_3O^+ . According to Hückel's theory, the mobility of D_3O^+ in D_2O should be very much lower than in the case of light hydrogen, since here the frequency of occurrence of the configurations for transfer is very much lower than for water, and might possibly be sufficient to reduce the mobility to the normal values for other ions of about the same size. Preliminary measurements have been made³

¹ E. Hückel, *Z. Electrochem.*, **34** (1928), 546.

² Bernal and Fowler, *loc. cit.*

³ G. N. Lewis and T. C. Doody, *J. Amer. Chem. Soc.*, **55** (1933), 3509.

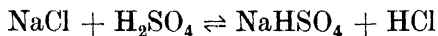
which show that, with D_3O^+ in D_2O , there is still an extra-normal mobility amounting to about one-half that for H_3O^+ in H_2O . This apparent disagreement may, however, quite well arise from the fact that the calculation of the frequency of very favourable configurations is very susceptible to small errors in the values of the physical constants which might be made particularly easily in the case of the deuterium ion in heavy water.

CHAPTER XII

IONIC EQUILIBRIA IN ACID AND BASE SOLUTIONS

Strengths of Acids and Bases.

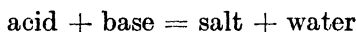
THE early chemists called all substances possessing a sour taste acidic, while those which, like plant ashes, destroyed the sour-taste property of acids giving salts were distinguished as "alkaline," the word "base" being used to denote the supposed fundamental metallic constituent of the alkali. Base metals were held to be responsible, therefore, for the above-mentioned characteristic of alkaline compounds, and in apposition to these, the "noble" metals could not be made to give any derivatives which possessed the property of "neutralising" the sour taste of acids. The arbitrary nature of these early definitions of acids and bases was very unsatisfactory, and attempts were made to draw up tables of the relative strengths of acids and bases by which it was hoped to find some clue to a more fundamental definition. These relative strengths were measured by the ability of one acid or base to displace another; for example, the fact that sulphuric acid was able to displace both hydrogen chloride and nitric acid from sodium chloride and from sodium nitrate, respectively, was considered sufficient evidence for asserting that sulphuric acid was the strongest of the three acids. Such an observation takes no account of the equilibrium set up—*e.g.*,



which may be disturbed by the removal of one of its components, in this case of the hydrogen chloride by its volatility, and in consequence seriously conflicting results were obtained. Thus the fact that hydrogen sulphide displaced sulphuric acid in copper sulphate, and yet was itself replaced by hydrogen chloride in ferrous sulphide, appeared to put the strengths

of hydrochloric and sulphuric acids in the reverse order to that observed in the displacement of the former from its salts by the latter. Moreover, the terms "strength" and "concentration" as applied to acids and bases, were confused, a "weak acid solution" being used to denote a solution of an acid of low relative strength and also of a dilute solution of any acid independent of its relative strength.

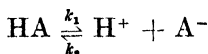
This confusion of definitions was temporarily solved by the advent of the Arrhenius theory of ionic dissociation. According to this, the "general" equation



became



and acids and bases could be defined, respectively, as compounds which gave hydriions and hydroxyl ions to their solutions. The dissociation theory in its simplest form was based upon the van 't Hoff equilibrium principle. In an ideally simple system of an acid dissociating into ions in solution, where each component, while free, behaves as if unaffected by the presence of other solutes or by molecules of the solvent, the dissociation equilibrium was written as



where k_1 and k_2 are, respectively, the mass constants for the forward and backward reactions. Now the mass-action principle is essentially a statistical law which assumes that the numbers of each of the different species present are so large that, over the instant during which the velocity is defined and hypothetically measured, the concentrations of the appropriate species remain sensibly constant. Applying it, with this reservation, to the above dissociation, the velocities of the forward and backward reactions were represented as :

$$v_1 = k_1(\text{HA}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (535)$$

$$v_2 = k_2(\text{H}^+)(\text{A}^-) \quad . \quad . \quad . \quad . \quad . \quad . \quad (536)$$

$$\text{i.e.,} \quad \frac{k_1}{k_2} = \frac{(\text{H}^+)(\text{A}^-)}{(\text{HA})} = K_{\text{acid}} \quad . \quad . \quad . \quad (537)$$

The quantity K_{acid} written with the concentrations of the ionic species in the numerator was called the dissociation constant of the acid, and represented the extent to which the equilibrium proceeded towards dissociation. The dissociation constants of different acids compared at equivalent concentrations were supposed, therefore, to constitute a quantitative measure of the strengths or "avidities" of these acids. In the case of the stronger acids, however, which, according to Arrhenius, were completely or almost completely dissociated, the term (HA) became so small that the values of the dissociation constant could not be measured with accuracy, and it was found more convenient to compare the strengths of the more highly dissociated acids by measuring their hydron concentrations in solutions of equivalent dilution. Although the method of E.M.F. measurement gives a fairly accurate estimate of the hydron concentration in a solution, the other method which was widely used—viz., measuring the influence of the acid on the course of reactions like the inversion of cane-sugar—failed to take account of the general acid and base catalysis of such reactions or of the spontaneous reaction velocity due to solvent effects. Methods were also proposed to determine the relative avidities of acids by observing some suitable quantity such as the heats of neutralisation or changes in volume, first with one equivalent of each acid treated with an equivalent of base, and then with a mixture of one equivalent of each acid added to one equivalent of the base. In the latter case when both acids competed for the same base, if the heat evolved were Q and the separate heats of neutralisation were Q_1 and Q_2 ,

$$Q = (1 - x)Q_1 + x \cdot Q_2 \quad . \quad . \quad . \quad (538)$$

x here denotes the distribution of the base between the acids, and it would therefore be a measure of the ratio of their avidities measured on any arbitrary scale.

It was significant that the results obtained for the relative strengths of acids (and also of bases) by these methods—viz., by measuring the E.M.F.'s of a standard cell having the acid

as one solution, by observing the catalytic effects on reactions in solution, and finally by determining the distribution coefficient—differed numerically often by as much as 20%. It must indeed be regarded as fortuitous that even the same order of relative strengths was obtained by the different methods for the commoner mineral acids when so equivocal a method as that employing catalytic effects was used, and when very little attention was given to comparing the results by the different methods at equivalent concentrations. In view of the modern theories of solution, however, which have eliminated the significance of the Arrhenius degree of dissociation, the emphasis which was at one time put upon the relative strengths of strong acids has shifted, and the problem of definition has again become predominant. For, according to the theory of complete dissociation, all "strong" acids will be equally "strong" over normal ranges of dilution if their strengths are represented in terms of their dissociation, and the question of ion association in terms of Bjerrum's ion pairs expressed quantitatively by the true degree of dissociation is one of secondary importance. Nevertheless, the concept of a dissociation constant as a relative measure of the strengths of weak acids and bases will retain its value for those substances which conform to the Ostwald dilution law, and whose properties in solution may still be adequately explained by the Arrhenius theory, in its simple form.

Catalytic Effects in Solutions and the Redefinition of Acids and Bases.

To assume that hydrions and hydroxyl ions are solely responsible for catalytic effects in solution, is not in agreement with the observed salt effects of catalytic phenomena. The addition of sodium acetate to a solution of cane sugar which is being inverted under the catalytic influence of hydrions should cause a decrease in the velocity of reaction by depressing the hydrion concentration, whereas a large increase in velocity is observed to take place. Arrhenius showed this effect on the inversion when the normal salts of acetic, formic, and phosphoric acids were added to a solution

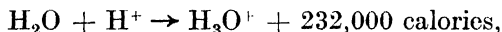
of cane sugar being inverted under the catalytic influence of the free acid, and he was able to show that the acceleration of the inversion was directly proportional to the quantities of salt added.¹ The simple differential equation :

$$-\frac{\partial[\text{C}_{12}\text{H}_{22}\text{O}_{11}]}{\partial t} = K_0 + K_1[\text{H}^+] \quad . \quad (539)$$

is therefore inadequate if it is to account for the "general acid and base catalysis" following from the catalytic effect which both sodium acetate molecules and the acetate ion must have had on the reaction. Even a dual theory of catalysis which supposed that neutral salts and their anions might also have catalytic effects² was not adequate to meet the experimental results, for the decompositions of many substances, such as diacetone alcohol (of alkalis), by solutions



are found to be favoured by dilution alone, and decomposition proceeds in solution in the absence of any neutral salt or of hydrions or hydroxyl ions.³ Here the solvent itself must then be capable of catalysing the reaction. Work on the hydration of ions (see p. 356) had shown that the hydrion was almost certainly H_3O^+ , for the heat which would be evolved in the reaction between H^+ and water was calculated by Fajans⁴ to be



showing that there would be very few H^+ ions in equilibrium with H_3O^+ ions in the solution. The evidence of Goldschmidt (see p. 357), adduced from the esterifications of organic esters in alcoholic solutions containing a little water, supported the view that hydrogen ions were present in the form H_3O^+ , and that there was no reason for supposing H_3O^+ was not the active catalyst of aqueous acid solutions. If, then, the hydrogen ion exists as H_3O^+ in aqueous solutions,

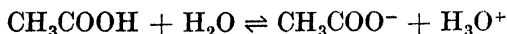
¹ Arrhenius, *Z. physikal. Chem.*, **31** (1899), 197.

² Dawson, *Trans. Faraday Soc.*, **24** (1929), 440; *J.C.S.* (1927), 2282, 2872, 3166; 213, 458, 256, 1146, 1290, 2107, 2444.

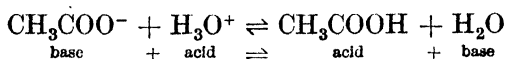
³ Kölichen, *Z. physikal. Chem.*, **33** (1900), 129.

⁴ K. Fajans, *Verh. Deutsch. Phys. Ges.*, **20** (1918), 209.

it shows no especial difference from other acids which can split off a proton in the presence of a proton acceptor—*e.g.*,



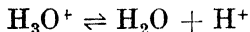
where the proton from the H_3O^+ ion is accepted by the acetate ion just as acetic acid surrenders its proton to the water molecule. In order therefore to co-ordinate all cases of acid and basic behaviour, Lowry and Brönsted¹ proposed that *acids be defined as proton donors, bases as proton acceptors*. These definitions allow for the analogous behaviour expressed by the forward and the reverse reactions



In these reactions CH_3COO^- and CH_3COOH are spoken of as a “conjugate pair” of acid and base, for the above reaction is the overall result from the two dissociations,

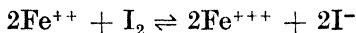


where CH_3COOH and CH_3COO^- form one pair of acid and base and

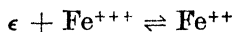


where H_3O^+ and H_2O form another pair.

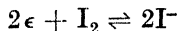
Such reactions show also a formal analogy with oxidation-reduction reactions of the type



which is the net reaction from the separate processes



and



Just as in the combined reactions of the oxidation-reduction reaction no electrons appear, so in the acid-base reaction no hydrogen ions appear as H^+ . Hydrated metal ions which are formed by many salts in aqueous solutions—*e.g.* :

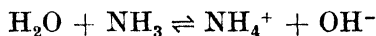


are able to split off hydrogen ions, so that they too must be regarded as acids. Here on Brönsted's definition a simple explanation is offered of their hydrolysis or acid reaction in aqueous solution.

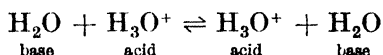
¹ Brönsted, *Rec. trav. chim.*, **42** (1923), 718.

Bjerrum has pointed out that the hydroxonium ion must be regarded as a tribasic acid, and he has calculated the relative influences of the three dissociation constants.¹

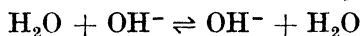
The example quoted of the reaction of acetic acid with water illustrates the behaviour of water as a base, but it may equally behave as an acid or proton donor towards a base, as in the reaction :



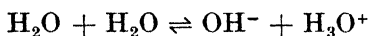
From its dual nature water may therefore be expected to behave acidically or basically towards itself, as expressed in the equations :



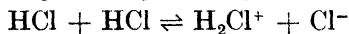
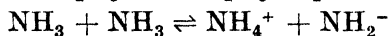
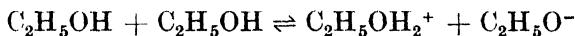
and



In the former, the water molecule acts as a proton acceptor (base) for the proton from H_3O^+ , while in the latter case the water behaves as a proton donor,—i.e., acidically—towards the negative OH^- . By analogy with the acetic acid case, these separate equations can be combined together to give :



Such equilibria between molecules of the same solvent are not confined to water alone, but may be set up in non-aqueous solutions, e.g.



in each of which cases the hydrogen is combined as an ion in quite different ways. In the last example given of hydrogen chloride, if the first hydrogen chloride molecule, acting as a proton acceptor, and being therefore only very weakly basic, is replaced by a water molecule which can behave as a powerful base or proton acceptor, the tendency to ionise increases enormously, as indeed is well known from observations of the conductivity. A similar case is observed from the behaviour of ammonia, which when quite pure is practically a non-

¹ Bjerrum, *Z. physikal. Chem.* (A), 106 (1923), 219.

conductor of electricity, but which in the presence of water (now behaving as a powerful proton donor) becomes a strong electrolyte. The acid and base dissociation constants of water are therefore equal to :

$$K_{\text{acid}} = \frac{[\text{H}_2\text{O}][\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]} = \frac{[\text{H}_2\text{O}][\text{OH}^-]}{[\text{OH}^-]} \\ = K_{\text{base}} = 55.55 \quad . \quad . \quad . \quad . \quad (540)$$

The figure 55.55 ($\frac{1000}{18}$) here denotes the number of gram-molecules of water per litre, and it is equal therefore to the molecular concentration. In many catalytic reactions the occurrence of a spontaneous reaction velocity in the absence of either added hydriions, hydroxyl ions, or of any neutral salt may therefore be ascribed to a solvent effect which is fundamentally similar to the cases of catalysis in the presence of other ions. This view is confirmed by the fact that the catalytic constant arising from the solvent effect factor is expressed quantitatively by the same empirical relationship as that obeyed by the other catalytic factors of general acid and base catalysis,¹ viz.,

$$K_{\text{catalytic}} = GK_{\text{acid or base}}^x \quad . \quad . \quad . \quad (541)$$

where x is a fraction less than unity and G and x are constant for a whole series of acids or bases. These generalised definitions of "acid" and "base" serve therefore to explain on an intelligible and uniform basis all the observed phenomena of catalysis of reactions in solution.²

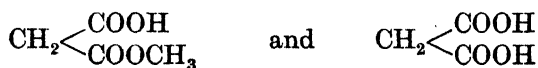
The Dissociation Constants of Acids and Bases.

As was seen for the case of hydrogen chloride, for which the ionisation is increased enormously by the presence of a stronger base like water, the strengths of acids and bases depend very much on the solvent chosen, and it is therefore

¹ Brönsted, *Trans. Faraday Soc.*, **24** (1928), 630.

² See, for example, J. N. Brönsted, "Acid and Base Catalysis," *Chem. Rev.*, **5** (1928), 231. "The extended theory of acid and base catalysis." Brönsted's definitions of acids and bases have been modified and extended by Bjerrum (*Chem. Rev.*, **16** (1935), 287), to include the case of salts. Wider definitions are introduced which allow the terms salt and base to be used only in a more restrictive sense.

imperative to compare the strengths of acids and bases *in the same solvent*. Other factors which help to determine the degree of dissociation of an acid or base have been investigated by Brönsted with the help of the cobaltammine ions, which are peculiarly suitable for experiments of this character (see the effect of salts on solubility, p. 204).¹ For an acid the dissociation will be higher the greater the positive charge on the molecule or the lower the negative charge, since the proton will then be more readily lost. When the molecule has a slight negative charge there is an increased tendency for any remaining ionisable hydrogens to be retained more firmly, as in the last stages of the dissociation of polybasic acids. In this connection, however, the dissociation of polybasic organic acids, which show the relationship generally, may among themselves show variations of parallel constants, due to complicating factors like steric effects (see p. 378), and the rule that a molecule possesses a more acidic character the higher its positive charge, is only a general one. By the same argument the basicity should also have a strong influence on the dissociation of an acid, for an acid containing two ionisable hydrogens, and therefore a high central positive charge, will have a higher first dissociation constant than one of similar structure containing only a single ionisable hydrogen. The difficulty, however, in attempting to verify this relation for polybasic acids is in the choice of a suitable series of similar structure, containing successively greater numbers of ionisable hydrogens. For example, it might at first be supposed that a series of organic acids like acetic, malonic and citric acids would be able to give confirmation to the rule, but these do not fulfil the condition requiring similarity of structure, and examples from the polycarboxylic acids would have to be confined to cases like



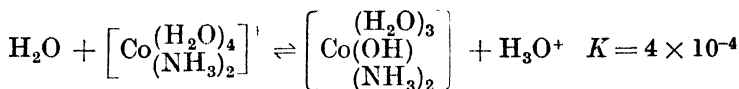
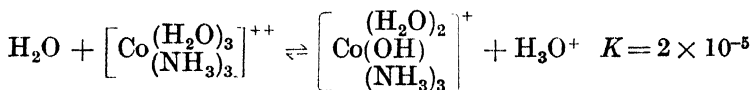
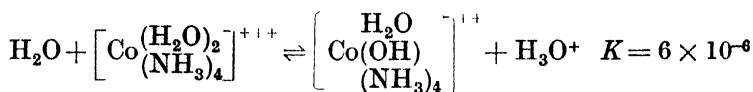
A better series for comparison is found among the aqua-

¹ Brönsted, *loc. cit.*, pp. 291–311, where original references are given.

Brönsted and Volquartz, *Z. physikal. Chem. (A)*, **134** (1928), 197.

Brönsted and King, *ibid.* (A), **130** (1927), 699.

ammine metal complexes, and Brönsted gives the following data from the cobaltammine series :



The relation between acid strength and the charge on the central atom may also be applied directly to explain the well-known increase in electronegative characteristics in progressing from the left to the right of the periodic table in one particular period. The acids from each element are, for this purpose, supposed to be formed from hydrated forms of the central atom reduced to the electron configuration of the *preceding* inert gas. Thus for chlorine at the right of the first short period, $\text{Cl}^{+7}(\text{H}_2\text{O})_4$ would immediately lose 7H^+ giving HClO_4 , and the tendency to pass to the *next* inert gas structure would be sufficiently great, in the case of chlorine, to cause the expulsion of the final hydrogen giving the completely dissociated $\text{H}\{\text{ClO}_4$. With sulphur, the hydrated ion $\text{S}^{+6}(\text{H}_2\text{O})_4$ would give H_2SO_4 by loss of 6H^+ , but here the sulphur is further from the next inert gas structure and nearer the structure of the last inert gas than is chlorine, so that the tendency to revert to $\text{H}_2\{\text{SO}_4$ is only slight and the stage

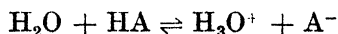


will be the only one taking place to any great extent.

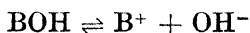
At magnesium (progressing leftwards across the second short period) the acidic properties will have become almost negligible, although aluminium shows them to a slight extent in the formation of aluminates from H_3AlO_3 , while the sodium ion with its single positive charge shows no perceptible acid forming properties.

The degree of dissociation of bases will be determined by an exact reversal of this condition, stronger basicity prevailing the lower the positive charge on the central atom in terms of the last inert gas structure or the higher its negative charge in terms of the next inert gas—*e.g.*, Na^+ or Na^{-7} . The volume of the central ion also has a considerable effect on the strengths of acids and bases, for the more compact the central ion, and the more intense its field, the less opportunity is there for hydrogen to dissociate from the structure. Strong acids will be those such as HClO_4 , where the field, due to the central ion, is diffuse. Since also, the greater the size of the atom, the more electrons it has in its electron shell, the order will be the same as that indicated by the charges on the central ion.

Returning now to the case of the dissociation of a weak acid or base represented for an acid by the equation



or for a base by



the equilibrium constant will be, in the first case

$$K = \frac{(\text{H}_3\text{O}^+)(\text{A}^-)}{(\text{H}_2\text{O})(\text{AH})} \quad . \quad . \quad . \quad (542)$$

where terms in parentheses represent activities, while quantities in brackets will be used to denote concentrations only. This, as already explained (see p. 366), is the reaction equation obtained by compounding two separate dissociations, one of the acid,



$$\text{with constant } K_{\text{acid}} = \frac{(\text{H}^+)(\text{A}^-)}{(\text{HA})} \quad . \quad . \quad (543)$$

the other of the solvent water in its basic character,



$$\text{for which } K_{\text{base}} = \frac{(\text{H}_3\text{O}^+)}{(\text{H}^+)(\text{H}_2\text{O})} \quad . \quad . \quad (544)$$

The tendency of the acid to ionise as represented by the compound equation, is therefore

$$\frac{(\text{H}_3\text{O}^+)(\text{A}^-)}{(\text{H}_2\text{O})(\text{HA})} = K_{\text{base}} K_{\text{acid}} \quad . \quad . \quad . \quad (545)$$

and this should strictly be the value calculated and quoted as the ionisation constant of the acid, since it shows the dependence of ionisation on the solvent. It is, however, convenient still to use the old expression for the dissociation constant of an acid—viz.

$$K_{\text{acid}} = \frac{(\text{H}^+)(\text{A}^-)}{(\text{HA})}$$

but although this expression is used freely in dealing with all problems of ionic equilibria, hydrolysis and indicators, it must be understood that it does *not* represent the true tendency of the acid to ionise, and it is used simply to denote what Arrhenius supposed by the dissociation constant of an acid or base. In the case of aqueous solutions, however, since the concentration of H^+ ion in equilibrium with the hydrated ion H_3O^+ is very minute the expression K_{acid} is a true measure of the real ionisation constant if (H^+) may be replaced by (H_3O^+) . For such a weak acid or base as that considered, the Arrhenius theory may be applied without introducing serious error and the degree of dissociation may be represented by α . If the initial dilution is V , then, to a first approximation, the "active masses" of the constituents in the acid dissociation at equilibrium will be equal to the concentration terms—i.e.:

$$\left. \begin{aligned} (\text{HA}) &\simeq \frac{1 - \alpha}{V} \\ (\text{H}_3\text{O}^+) \text{ and } (\text{A}^-) &\simeq \frac{\alpha}{V} \end{aligned} \right\} \dots \dots (546)$$

$$\text{i.e.,} \quad K_{\text{acid}} = \frac{\alpha^2}{(1 - \alpha)V} \dots \dots (547)$$

to a first approximation.

This relation has been used by Ostwald to calculate the dissociation constants of weak acids and bases,¹ since values of αA are available from conductivity measurements and A_∞ may be determined by Kohlrausch's law of independent mobilities. The values of the constants were shown by Ostwald to be fairly consistent up to quite moderate dilutions for the weaker acids and bases. This agreement, however,

¹ W. Ostwald, *Z. physikal. Chem.*, 3 (1889), 120, 241, 369.

was probably due, in part at least, to the compensation of two effects. Arrhenius' method for computing degrees of dissociation gives values which are too low, and the activity coefficients, which were tacitly assumed to be unity, are in reality less than one, so that this difference will affect the calculated dissociation constant in the opposite sense. Actually the activity coefficients of the ions even in dilute solutions are quite far removed from unity,¹ and the Ostwald-Arrhenius dissociation constants may be widely at variance with the true values.

The True Ionisation Constant of an Acid.

A simple application of the theory of interionic attraction allows an expression to be obtained for the true ionisation constant. Debye has calculated the effect of interionic electrostatic forces on the activity coefficients of ions, and his results show that at 25° C. for aqueous solutions of uni-univalent electrolytes (see equation 304).

$$\log f = -0.505 \sqrt{\gamma}$$

over a limiting and very narrow range of high dilutions (this neglects Debye and Hückel's second approximation or any other extension of the simple theory). If expressions such as $[H_3O^+]$ are used to denote concentration terms, the dissociation constant is therefore :

$$K_{\text{acid}} = \frac{f_{H_3O^+} f_{A^-}}{f_{HA}} \cdot \frac{[H_3O^+][A^-]}{[HA]} \quad . \quad . \quad (548)$$

$$\text{where } [H_3O^+] = [A^-] \quad . \quad . \quad . \quad (549)$$

and using equation (304) :

$$\begin{aligned} \log (f_{H_3O^+} f_{A^-}) &= -2 \times 0.505 \sqrt{[H_3O^+]} \\ &= 1.010 \sqrt{c} \text{ at } 25^\circ \text{ C.} \quad . \quad . \quad . \quad (550) \end{aligned}$$

Thus from (548)

$$\log \frac{[H_3O^+]^2}{[HA]} = \log K_{\text{acid}} + 1.010 \sqrt{c} \quad . \quad . \quad (551)$$

$$\text{or} \quad \log K_{\text{acid}} = \log [K]_{\text{acid}} - 1.010 \sqrt{c} \quad . \quad . \quad (552)$$

$$\text{where} \quad [K]_{\text{acid}} = \frac{[H_3O^+][A^-]}{[HA]}$$

¹ D. A. MacInnes, *J. Amer. Chem. Soc.*, **58** (1936), 2068.

the quantities in square brackets representing concentration terms and not active masses. It should therefore be possible to determine the true equilibrium dissociation constant of an acid (or base) if the concentration term $[H_3O^+]$ or $[A^-]$ can be determined at equilibrium. Measurements have been made by this method with a view to determining the dissociation constant of acetic acid.¹ In order to find α^* , the true degree of dissociation, the equivalent conductivities at a concentration c and at infinite dilution are used. These are respectively :

$$\text{and} \quad \left. \begin{aligned} \Lambda_c &= \alpha^*[u_c + v_c] \\ \Lambda_\infty &= [u_\infty + v_\infty] \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (553)$$

It follows that

$$\alpha^* = \frac{\Lambda_c}{\Lambda_\infty} \quad . \quad . \quad . \quad . \quad . \quad . \quad (554)$$

only if the ionic mobilities are unchanged over the range of concentrations c to infinite dilution. Changes in the ionic mobilities are, however, to be expected from Onsager's calculation of the effect of interionic forces on a moving ion and the original Arrhenius equation (4)

$$\alpha = \frac{\Lambda_c}{\Lambda_\infty}$$

will therefore not be true at any dilution. If, however, the expression

$$\Lambda_c = u_c + v_c \quad . \quad . \quad . \quad . \quad (555)$$

be used where Λ_c would be the conductivity due to the ions at concentration c if the substance were completely dissociated, then α^* may be calculated, for it is then given by

$$\alpha^* = \frac{\Lambda_c}{\Lambda_\infty} \quad . \quad . \quad . \quad . \quad . \quad (556)$$

For acetic acid, represented as HAc, we may write :

$$\Lambda_{c,HAc} = \Lambda_{c',HAc} - \Lambda_{c',NaCl} + \Lambda_{c',NaAc} \quad . \quad . \quad (557)$$

$\Lambda_{c,HAc}$ being the equivalent conductivity of completely ionised acetic acid at the ion concentration c' . For a computa-

¹ MacInnes and Shedlovsky, *J. Amer. Chem. Soc.*, **54** (1932), 1429.
MacInnes, Shedlovsky, and Longworth, *Nature*, **130** (1932), 774.
M. A. Sherill, and Noyes, *J. Amer. Chem. Soc.*, **48** (1926), 1861.

tion of α^* , therefore, a value of A_c must be found which corresponds to the ion concentration of the solution of the weak acid, the measured equivalent conductance of which is A_c , and this involves a short series of approximations. Carefully measured values¹ of the conductivity terms involved in equation (557) have been used to calculate the acid dissociation constant of acetic acid, and some of the results obtained at 25° C. are quoted in Table XI. Here K_{acid} is the dissociation constant as measured at different concentrations and $[K]_{\text{acid}}$ that calculated from the Ostwald formula, assuming from equation (4) that

$$\alpha = \frac{A_c}{A_\infty}$$

and that the activity terms could be replaced by concentrations.

TABLE XI.

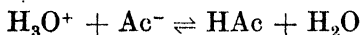
Acid Dissociation Constant of Acetic Acid.

Total conc.	Ion conc.	A_c .	A_∞ .	$K_{\text{acid}} \times 10^5$.	$[K]_{\text{acid}} \times 10^5$.
0.028014	0.15107	390.02	210.32	1.7522	1.7682
1.02831	1.2727	388.94	48.133	1.7508	1.7974
12.829	4.7591	387.41	14.371	1.743	1.834
200.000	18.992	384.41	3.650	1.645	1.821

The data corresponding to solutions of acetic acid below 0.01*N* are in quantitative agreement with equation (552) :

$$\log K_{\text{acid}} = \log [K]_{\text{acid}} - 1.010 \sqrt{c}$$

but above that concentration a strong "medium effect" due to a change in activity of the solvent in the equation



becomes apparent and influences the ionic mobilities.

Similar measurements of the true ionisation constant of a weak acid have been made on the first-stage dissociation of carbonic acid :



¹ Values obtained by Shedlovsky's bridge method (see p. 66).
J. Amer. Chem. Soc., **52** (1930), 1793.

a reaction which is of considerable importance in biochemistry.¹ The thermodynamic ionisation constant K for this reaction is given by the equation

$$K = \frac{c\alpha^{*2}f^2}{(1-\alpha^*)} \cdot \cdot \cdot \cdot \cdot \quad (558)$$

where α^* , the true degree of ionisation, is given by the expression Λ_c/Λ , as before, and c is the concentration. Λ_c the equivalent conductance of the carbonic acid which would be observed if this were completely dissociated as a monobasic acid, was computed from measurements of the conductivity of hydrochloric acid, potassium chloride, and potassium hydrogen carbonate using the relation

$$\Lambda_{c,H_2CO_3} = \Lambda_{c,H+Cl-} - \Lambda_{c,K+Cl-} + \Lambda_{c,K+HCO_3-} \quad (559)$$

all the conductivities being measured at a concentration $c\alpha^*$. The measurements were carried out over a range of temperatures from 0° C. to 38° C., and the results obtained (Table XII) show how sensitive are the values of ionisation constants to temperature.

TABLE XII.

First Dissociation Constant of Carbonic Acid.

Temperature. ° C.	Concentration.	Λ_c .	Λ .	f^2 .	$K_1 \times 10^6$.
0	6.03284	0.7040	247.2	0.9785	3.613
15	6.03282	1.1410	335.4	0.9764	3.722
25	6.03275	1.4401	392.6	0.9746	4.310
38	6.03262	1.8040	464.0	0.9743	4.817

The Dissociation Constants of Polybasic Acids.

Polybasic acids dissociate in stages, and the various stages of dissociation each have a separate dissociation constant. Usually the values for the dissociation constants after the first stage are very much smaller than the first-stage constant, and examples from the dibasic organic acids measured by

¹ Shedlovsky and MacInnes, *J. Amer. Chem. Soc.*, **57** (1935), 1705.
Cf. MacInnes and Belcher, *ibid.*, **55** (1933), 2630.

Ostwald,¹ Chandler² and Wegscheider³ show this effect very well.⁴

Ostwald's measurements on the conductivities of these dibasic acids showed that the values of K_1 , calculated from the dilution law, maintained their constancy up to very high dilutions, and he explained this by supposing the negative

TABLE XIII.

Dissociation Constants of Some Polybasic Acids.

Acid.	Temp., ° C.	Range of concentration.	Constant.	Author.
Azelaic acid	25	68-1091	$K_1 = 2.5 \times 10^{-5}$	Smith
	25	32-4096	$K_2 = 2.4 \times 10^{-6}$	Chandler
Maleic acid	25	32-2048	$K_1 = 1.2 \times 10^{-2}$	Ostwald
	25	32-4096	$K_2 = 2.6 \times 10^{-6}$	Chandler
Fumaric acid	35	32-2048	$K_1 = 1.0 \times 10^{-3}$	—
	25	32-4096	$K_2 = 3.0 \times 10^{-5}$	Chandler
Succinic acid	25	8-2048	$K_1 = 6.6 \times 10^{-5}$	Ostwald
	25	32-4096	$K_2 = 2.8 \times 10^{-6}$	Chandler
Acetomethylamino- terephthalic acid	25	150-2048	$K_1 = 1.4 \times 10^{-3}$	Wegscheider
	25	150-2048	$K_2 = 5.0 \times 10^{-5}$	Wegscheider
Dibromosuccinic acid	25	32-4096	$K_1 = 3.4 \times 10^{-2}$	Chandler
	25	32-4096	$K_2 = 1.6 \times 10^{-3}$	Chandler

charge retained on one COO^- group, after the first stage of dissociation had taken place, caused the second proton, with its positive charge, to be held more firmly. Such an hypothesis will account for the lower dissociation constants of all polybasic acids in their higher stages of dissociation—e.g., in citric acid for which at 25° C. $K_1 = 8.1 \times 10^{-4}$, $K_2 = 1.7 \times 10^{-5}$ and $K_3 = 4.0 \times 10^{-6}$.⁵

This explanation may also be extended to account for the greater values of the second dissociation constants of

¹ Ostwald (conductivity method), *Z. physikal. Chem.*, **3** (1889), 170, 241, 369.

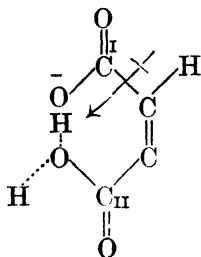
² Chandler (conductivity and partition coefficient method), *J. Amer. Chem. Soc.*, **30** (1908), 394.

³ Wegscheider (conductivity of the free acid), *Monatsh.*, **37** (1916), 219.

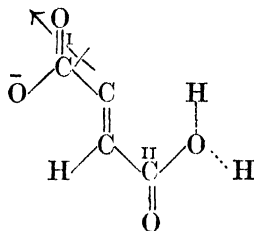
⁴ The values given in Table XIII are quoted from Landolt-Börnstein (5 Auflage, § 221).

⁵ From measurements by Bjerrum and Unmack, *Det Kgl. Danske Videnskab. Selskab.*, **9** (1929), 1.

trans dibasic unsaturated acids as compared with the *cis* acids. It has been seen from the values quoted in the table above that K_2 for maleic acid is 2.6×10^{-6} , whilst the corresponding constant for fumaric acid is 3.0×10^{-5} . If account be taken of the steric arrangement of the two acids after the first-stage dissociation, the following dispositions will occur, at some instant during the free rotations of the carboxyl groups:



For ionised maleic acid.



For ionised fumaric acid.

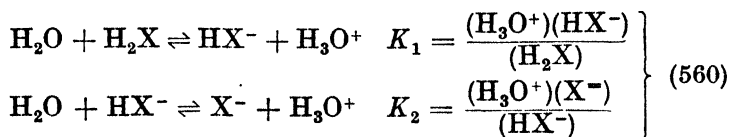
(Here the dotted OH positions indicate the extreme positions during rotation of the $\geq C^{\text{II}}-O$ link.) In the former of these, the ionisable hydrogen is on an average much more directly under the influence of the dipole associated with the $\geq C^{\text{I}}-O^-$ link and marked in by the arrow (the head of the arrow being its negative end), than in fumaric acid. This is particularly the case, as, in maleic acid, the large oxygen atoms which are doubly bound to the carbons will tend to inhibit any free rotation of the carboxyls which might place them in such a disposition that the ionisable hydrogen was a long way from the influence of the dipole. The residual hydrogen in singly ionised maleic acid will therefore be quite firmly held, and only at the highest dilutions in solvents of high dielectric constant will the electrostatic attraction cease to overcome the energy of vibration of the remaining hydrogen and allow ionisation to occur. The conditions in ionised fumaric acid, however, are such that free rotation of the carboxyl group II is quite possible, and the average effect of the dipole will be approximately in the direction shown.¹

¹ This assumes that resonance, which would be possible here due to the allowed free movement of the electrons involved, does not

The remaining ionisable hydrogen will therefore always be at the positive end of the dipole and well away from this, so that any influence which this may have will be a repulsion due to a direct electrical effect. These factors will combine therefore to account for the much smaller second dissociation constant of a *cis* dibasic unsaturated acid compared with that of the corresponding *trans* acid.

Measurement of Second Dissociation Constants of Polybasic Acids.

Whereas the measurement of the first dissociation constant of dibasic acids presents no difficulty, since second-stage dissociation rarely becomes appreciable until first-stage dissociation is more than 50% complete, the determination of the second dissociation constant is a much more difficult problem. For, at dilutions where the second stage becomes appreciable, the first stage is large, but still not complete. Chandler ¹ overcame this difficulty by carrying out measurements similar to those used to give the first constant, on the acid salts of the dibasic acids, where the dissociation of the salt corresponding to the first stage dissociation of the acid is practically complete and the second stage has become important. The method was first used by McCoy ² for measuring the second dissociation constant of carbonic acid. The two stages of dissociation of a dibasic acid are :



An acid salt, on the other hand, reacts in water forming partly the free acid and partly the neutral salt, so that

$$\frac{(\text{NaHX})^2}{(\text{H}_2\text{X})(\text{Na}_2\text{X})} = \frac{(\text{HX}^-)^2}{(\text{X}^{2-})(\text{H}_2\text{X})} = \frac{K_1}{K_2} \quad (561)$$

take the place of free rotation. In either case the average effect of the dipoles will be the same. In maleic acid, resonance would be prevented from occurring since the electrons would be constrained here to vibrations about their mean positions, due to the proximity of the OH group.

¹ E. E. Chandler, *J. Amer. Chem. Soc.*, **30** (1908), 694.

² McCoy, *ibid.*, **30** (1908), 688.

To determine the position of the equilibrium, it is necessary to know the activity of the undissociated acid (H_2X), and if it is assumed that this may be given by the product of the measured concentration of the acid $[H_2X]$ and the activity coefficient calculated for the appropriate ionic strength from the Debye expression, two methods are available for the determination of (H_2X). The concentration of the free acid $[H_2X]$ may first be determined by a partition method in which an aqueous solution of the acid salt is shaken with an immiscible or partially miscible solvent such as ether, in which the acid neither associates (as in chloroform) nor dissociates (as in the alcohols). From the concentration of the acid in the ethereal layer, the partition coefficient then gives the concentration of free acid *in the molecular form* in the aqueous layer. The total concentration of the basic constituent is known, and this, with the total acidity found by titration, gives HX^- and $X^{=}$.¹ These concentration terms, multiplied by the appropriate activity coefficients, will give K_1/K_2 , and since K_1 , the first-stage constant, is already known from conductivity measurements, K_2 may be determined.

The other method which has been used for estimating the second dissociation constant, makes use directly of the equation

$$K_2 = \frac{(H_3O^+)(X^{=})}{(HX^-)}$$

As applied by Chandler the method required the adoption of an arbitrary procedure in order to estimate the true equivalent conductivity of the acid salt, but this may be avoided by using ionic mobility data. With this modification the method has been used to determine the dissociation constant of the HSO_4^- ion from conductivity measurements on sodium hydrogen sulphate.² The equivalent conductivity of the HSO_4^- ion at the prevailing ionic strength, is given by :

$$\Lambda = \lambda_{Na^+} + (1 - \alpha)\lambda_{H_3O^+} + 2\alpha\lambda_{SO_4^{=}} \quad (562)$$

¹ For the expressions giving these terms see McCoy's paper.

² M. A. Sherill and A. A. Noyes, *J. Amer. Chem. Soc.*, **48** (1926), 1861.

where α is the degree of dissociation. The exact data for the equivalent conductivity of the HSO_4^- ion were not at the time available, and it was therefore necessary to determine this from the molecular conductivities of sulphuric acid solutions measured at different concentrations; if α^* is the degree of dissociation, and $\lambda_{\text{H}_2\text{O}^+}$, $\lambda_{\text{HSO}_4^-}$, and $\lambda_{\text{SO}_4^{2-}}$ represent the molecular conductivities of the relevant ions at the ionic strength of the solution, then the molecular conductivity of sulphuric acid is given by :

$$2\Lambda = (1 + \alpha^*)\lambda_{\text{H}_2\text{O}^+} + (1 - \alpha^*)\lambda_{\text{HSO}_4^-} + 2\alpha^*\lambda_{\text{SO}_4^{2-}} \quad (563)$$

Also since the transport number of hydron n_{H} , is equal to the number of equivalents of hydrogen migrating into the cathode liquid less the number of equivalents of HSO_4^- migrating out of the cathode liquid, we have :

$$n_{\text{H}} = \frac{(1 + \alpha^*)\lambda_{\text{H}_2\text{O}^+} - (1 - \alpha^*)\lambda_{\text{HSO}_4^-}}{2\Lambda} \quad (564)$$

i.e., from (563) and (564)

$$\lambda_{\text{HSO}_4^-} = \frac{\Lambda - \Lambda n_{\text{H}} - \alpha^*\lambda_{\text{SO}_4^{2-}}}{1 - \alpha^*} \quad (565)$$

where from equation (563)

$$\alpha^* = \frac{\Lambda + \Lambda n_{\text{H}} - \lambda_{\text{H}_2\text{O}^+}}{\lambda_{\text{H}_2\text{O}^+} + \lambda_{\text{SO}_4^{2-}}} \quad (566)$$

The values of $\lambda_{\text{SO}_4^{2-}}$ and $\lambda_{\text{H}_2\text{O}^+}$ at the prevailing ionic strength can be determined from measurements of the transport numbers of these ions in strong electrolytes—e.g., in HCl and K_2SO_4 at various concentrations, and α^* can therefore be found. Then :

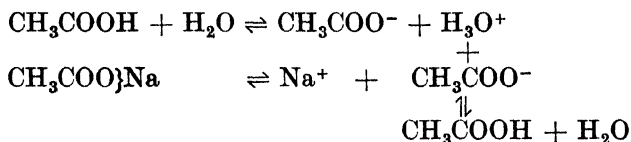
$$K_2 = \frac{a_{\text{H}_2\text{O}^+} + a_{\text{HSO}_4^-} - \alpha^{*2}c}{(1 - \alpha^*)} \quad (567)$$

in which the values of the ionic activities are calculated at concentrations where the ionic strengths are small, so that the Debye equation (304) can be applied without introducing serious error.

The Common Ion Effect.

One important case of the dissociation of weak bases and weak acids arises in connection with the theory of

qualitative analysis, viz., the so-called "common ion effect." If to a solution of acetic acid be added one of an electrolyte containing a common ion—*e.g.*, sodium acetate—the two equilibria present in solution react upon one another in accordance with the following equations :



The large excess of acetate ions provided by the sodium acetate so materially alters the active mass term (CH_3COO^-) in the solution that, in order to keep the function

$$K_{\text{acid}} = \frac{(\text{CH}_3\text{COO}^-)(\text{H}_3\text{O}^+)}{(\text{CH}_3\text{COOH})}$$

constant, the term (H_3O^+) must be correspondingly decreased. Were it not for the fact that sodium acetate is completely dissociated, so that there is no tendency for CH_3COO^- ions from acetic acid to combine with Na^+ ions, there would have been a corresponding reduction in the degree of ionisation of the added component and, in the general case of two electrolytes containing a common ion, each only partially dissociated—*e.g.*, two weak acids added one to the other—the degree of ionisation of each is decreased. The special case illustrated above by acetic acid added to sodium acetate, in which one of the electrolytes is completely dissociated, constitutes the principle of buffer action, and equations for the hydrion concentrations in such solutions of a weak acid or a weak base and its salt are deduced later in connection with the theory of indicators (see p. 448).

Arrhenius ¹ showed, however, that by mixing together two weak electrolytes containing a common ion, it should not always follow that a decrease in ionisation of both constituents should take place. It might, for example, be possible to obtain two solutions such that on mixing, the decrease in ionisation of one which would be caused by the addition of the other would be just equal to the increase in ionisation due to the increase in the volume of the solution

¹ Arrhenius, *Z. physikal. Chem.*, 2 (1885), 284.

which each electrolyte would separately undergo. The condition for this state of affairs was deduced by Arrhenius for the case of two weak acids HA_1 and HA_2 , which have degrees of ionisation α_1 and α_2 when in their initial solutions at dilutions V_1 and V_2 . Their dissociation constants will be given by the two Ostwald equations :

$$\left. \begin{aligned} K_1 &= \frac{\alpha_1^2}{(1 - \alpha_1)V_1} \\ \text{and} \quad K_2 &= \frac{\alpha_2^2}{(1 - \alpha_2)V_2} \end{aligned} \right\} \quad . \quad . \quad . \quad (568)$$

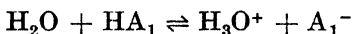
if it is assumed that active masses in the expressions for K_{acid} may be written as concentration terms. If the required condition is to be fulfilled, the degree of ionisation of each must remain unchanged by dilution and the final concentration of the hydrion will be given by :

$$[H_3O^+] = \frac{\alpha_1 + \alpha_2}{V_1 + V_2} \quad . \quad . \quad . \quad (569)$$

(providing no change in volume occurs from $V_1 + V_2$ when the two solutions are mixed). Similarly the final concentrations of the acid ion and the undissociated acid, will be :

$$\left. \begin{aligned} [A_1^-] &= \frac{\alpha_1}{V_1 + V_2} \\ [HA_1] &= \frac{\alpha_2}{V_1 + V_2} \end{aligned} \right\} \quad . \quad . \quad . \quad (570)$$

Thus for the dissociation



in the final solution, the dissociation constant is :

$$K_1' = \frac{[H_3O^+][A_1^-]}{[HA_1]} = \frac{(\alpha_1 + \alpha_2)}{(1 - \alpha_1)(V_1 + V_2)} \quad (571)$$

A similar expression to (571) is obtained for the dissociation constant of the second acid in the final solution. For the required condition to be fulfilled, therefore, since $K_1 = K_1'$ and $K_2 = K_2'$:

$$\left. \begin{aligned} \frac{(\alpha_1 + \alpha_2)_1}{(1 - \alpha_1)(V_1 + V_2)} &= \frac{\alpha_1^2}{(1 - \alpha_1)V_1} \\ \text{and} \quad \frac{(\alpha_1 + \alpha_2)}{(1 - \alpha_2)(V_1 + V_2)} &= \frac{\alpha_2^2}{(1 - \alpha_2)V_2} \end{aligned} \right\} \quad . \quad (572)$$

Both these equations by simplification, give,

$$\frac{\alpha_1}{V_1} = \frac{\alpha_2}{V_2} \quad . \quad . \quad . \quad . \quad . \quad (573)$$

or
$$[\text{H}_3\text{O}^+]_{\text{I}} = [\text{H}_3\text{O}^+]_{\text{II}} \quad . \quad . \quad . \quad (574)$$

The condition, therefore, that on mixing aqueous solutions of two weak electrolytes having a common ion, no change shall occur in the degree of dissociation of either, is that both shall possess initially the same concentration (or strictly the same active mass) of the common ion—*i.e.*, for the two acids considered, which have hydrogen as their common ion, they must possess the same concentrations of hydrion. Such solutions are therefore known as *isohydric* solutions.

Ionisation in Mixtures of Electrolytes.

The general principle (of which the above is a special case) which governs the degrees of ionisation of all mixtures of all electrolytes in aqueous solutions was deduced and formulated by Arrhenius as follows :

“In a mixture of two electrolytes with a common ion, each electrolyte has a degree of ionisation equal to that which it has when present alone in a solution where its ions have a concentration equivalent to that of the common ion in the mixture.”

Arrhenius had shown this to be obeyed, in the case of uni-univalent electrolytes, from conductivity measurements, and had confirmed the theory for ammonium hydroxide and ammonium chloride by observing the effect of adding ammonium chloride during the saponification of ethyl acetate by ammonium hydroxide.¹ Its applicability to other ionic types was confirmed experimentally by transport number measurements using the method of Washburn (p. 120) to determine the separate conductivities of the ions in the mixture.² Thus in a mixture of potassium sulphate and chloride the transport numbers of the anions, which

¹ Arrhenius, *loc. cit.*

² See also D. A. MacInnes, *J. Amer. Chem. Soc.*, **43** (1921), 1221, 1223.

represent the numbers of equivalents of SO_4^{--} and Cl^- transferred per faraday, are :

$$n_{\text{Cl}^-} = \frac{\text{specific conductivity of anion}}{\sum \text{specific conductivities of all ions}} = \frac{\gamma_{\text{Cl}^-} \lambda_{\text{Cl}^-}}{\sum} \text{ (say) } \quad (575)$$

(the γ 's representing equivalent concentrations and the λ 's the equivalent conductivities of the ions in the mixture) and

$$n_{\text{SO}_4^{--}} = \frac{A_{\text{SO}_4^{--}} \times \gamma_{\text{SO}_4^{--}}}{\sum} \quad (576)$$

$$\text{i.e., } \frac{n_{\text{Cl}^-}}{n_{\text{SO}_4^{--}}} = \frac{\gamma_{\text{Cl}^-} A_{\text{Cl}^-}}{\gamma_{\text{SO}_4^{--}} \lambda_{\text{SO}_4^{--}}} = \frac{\gamma_{\text{KCl}} \alpha_{\text{KCl}} \lambda_{\text{Cl}^-}}{\gamma_{\text{K}_2\text{SO}_4} \alpha_{\text{K}_2\text{SO}_4} \lambda_{\text{SO}_4^{--}}} \quad (577)$$

the α 's denoting degrees of ionisation. Knowing the transport numbers and the equivalent conductivities, it is possible to obtain values for the α 's and to compare these with the values calculated from equation (4)

$$\alpha = \frac{A}{A_{\infty}}$$

where A is the equivalent conductivity of each electrolyte at the concentration equal to that of the common ion in the mixture. The following table gives the results which were obtained, for mixtures of potassium chloride and sulphate.

TABLE XIV.

Dissociation in Mixtures of Electrolytes.

Expression Measured.	Calculated value ($\alpha = \frac{A}{A_{\infty}}$).	Experimental value.
Partial specific conductivity of KCl in mixture	0.02102	0.02093
Partial specific conductivity of K_2SO_4 in mixture	0.01587	0.01559
Ratio	1.325	1.342
Degree of ionisation of KCl in mixture	0.814	—
Degree of ionisation of K_2SO_4 in mixture.	0.595	—
Ratio	1.351	1.372

When it is remembered that the general principle stated above is deduced on the assumption that the Arrhenius theory may be applied to the equilibria between two electrolytes uncorrected for interionic effects or for the errors introduced by using concentration terms in place of activities, it is remarkable that so close an agreement is observed for two such salts as potassium chloride and sulphate. The experimental method for determining the degrees of ionisation does not, however, involve any specific theories of solution, and the use of Washburn's method for determining transport numbers avoids the inherent difficulties of the ordinary analytical methods and the corrections which must be made in moving boundary methods for the change in concentration of the solution at the electrodes, when a stationary solvent is not used (p. 120).

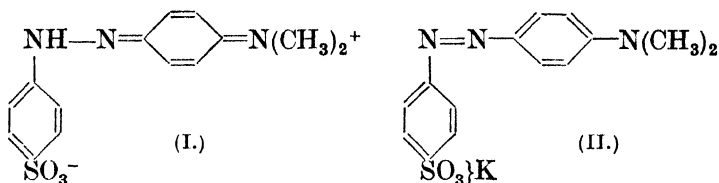
Amphoteric Electrolytes and Zwitterions.

It has been shown that water may behave either as an acid or as a base, while being itself neutral, and that such behaviour is not confined only to water, but is exhibited by other solvents, the acid or base properties appearing according to the solute added (see pp. 365-368). These substances are said to be "amphoteric" in behaviour, and compounds belonging to this class are particularly common and important among certain groups of organic substances which, although neutral themselves, contain acidic and basic functions and are able in solution to give rise to both positive and negative ions. This characteristic property is reflected in their chemical and physico-chemical properties. The existence of the group was, in fact, first illustrated by Walker¹ from the observation that they all failed to conform to Ostwald's dilution law, a fact which he attributed to the impossibility of representing their degree of dissociation by the Arrhenius expression (4).

By an investigation of the two-colour indicator properties of one member of the group—viz., methyl orange—a substituted monazo sulphanilic acid, it was shown by

¹ J. Walker, *Z. physikal. Chem.*, **57** (1907), 603.

Küster¹ that its structure would have to be different in acid and alkaline solutions. In acids it would have to possess a quinonoid structure (I) which was associated with the red colour while in alkalis, it would have to form a salt with the yellow-donating azo structure (II).



Methyl orange has the same red colour in the solid as its solution has in acid media, and it appears probable, therefore, that, in the solid, the molecule has a positive charge residing at one end and a negative charge at the other end. Küster therefore proposed to call this type of structure a "zwitterion," and the term will be used throughout the following discussion² for all structures having both positive and negative charges associated with different groups in the complex. Walker must have realised the possibility of such a structure for the then-known amphoteric electrolytes which were mainly amino-acids, for he wrote,³ "Die weitere Komplikationen durch Annahme eines Zwitterions $^+\text{NH}_3\text{CH}_2\text{COO}^-$ brauch nicht betrachtet zu werden da bei dem gegenwärtigen Stand unsere Kenntnisse über amphotere Elektrolyte diese Annahme nicht zur Erklärung der beobachteten Erscheinungen nötig ist." The idea of extending Küster's zwitterion structures to the amino-acids was, however, revived first by Adams⁴ and later by Bjerrum,⁵ who pointed out that the physical and chemical properties of the amino-acids show that they possess much more of a salt-like than an acid character. They have higher melting points than the ordinary organic acids of

¹ Küster, *Z. anorg. Chem.*, **13** (1897), 135.

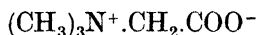
² The discussion of the dissociation properties of zwitterions in the following section, follows the principles laid down by Niels Bjerrum, *Z. physikal. Chem.*, **104** (1923), 147.

³ J. Walker, *ibid.*, **57** (1907), 603.

⁴ E. Q. Adams, *J. Amer. Chem. Soc.*, **38** (1916), 1503.

⁵ Bjerrum, *loc. cit.*

similar molecular complexity, and their solubility in non-polar solvents of low dielectric constant is small. An elegant confirmation of this structure theory for amino-acids is afforded from purely chemical evidence in the behaviour of ordinary betaine or trimethylglycine which, when dry distilled, loses trimethylamine. Reactions in which a methyl group wanders from a carbon to a nitrogen are very rare, and it is doubtful if this process could occur in a compound like betaine. The loss of trimethylamine from betaine by distillation would appear, therefore, to support the view that in this compound all the methyl groups are already attached to the nitrogen, in accordance with the formula



analogous to that which Bjerrum and Walker postulated for glycine itself.

A further and very convincing argument in favour of a zwitterion structure for the amino-acids is furnished by measurements of the dielectric constants of their solutions. No theory of the dielectric properties of polar solutions has yet been worked out which is entirely satisfactory, but the very high dielectric constants of these solutions are approximately additive,¹ and they can only be explained by attributing very high dipole moments of the order 20×10^{-18} E.S.U. to an amino-acid molecule. Even larger values are necessary when the charged groups are widely separated, as in the higher ω -amino-acids. Such high moments must be a consequence of a separation of the charges within the molecule such as a zwitterion structure has postulated. Assuming that this is the correct structure, the dipole moment may be expressed as the product of the electronic charge at either end of the molecule multiplied by the distance of separation r of the charges. Estimates of this dipole distance will therefore allow a calculation of the dipole moment to be made. Approximate values for the distance r may be obtained from X-ray measurements on the

¹ P. Girard, *Trans. Faraday Soc.*, **30** (1934), 763.

J. Wyman, *J. Amer. Chem. Soc.*, **56** (1934), 536; *Chem. Rev.*, **19** (1936), 213.

Wyman and McMeekin, *J. Amer. Chem. Soc.*, **55** (1933), 915.

crystals of amino-acids. Unfortunately it does not necessarily follow that the values of r so determined are the same as those involved when the molecules are in solution.

An alternative method for estimating the magnitude of the dipole distance in the amino-acids is made evident from the following considerations.¹ The effect of the charge of the amino-group on the dissociation constant is divided into a first fraction due solely to the charge effect of the new group, which is transmitted only by the dielectric properties of the solvent, and a second fraction due to the "chain effect" which is transmitted by the electronic deformations of each atom down the carbon chain between the amino- and the carboxylic groups. Now, the free energy of ionisation is related to the dissociation constant by equation (171)

$$F = RT \ln K$$

The magnitude of the chain effect cannot be directly estimated with any certainty and in order therefore to eliminate it, two sets of measurements must be made on the dissociation constant, first in a solvent I of dielectric constant D_I , then in a second solvent II of constant D_{II} . The electrical work gained by removing a proton from the carboxylic group will be given by :

$$w + \phi = e\psi \quad . \quad . \quad . \quad . \quad (578)$$

where ϕ is the molecular increment in free energy due to the chain effect, and ψ is the potential at the dipole distance due to the charged substituent. Assuming, with Bjerrum, that there is no Debye-Hückel effect and no change in the dielectric constant of the solvent due to the presence of zwitterions, we have :

$$\psi = \frac{e}{Dr} \quad . \quad . \quad . \quad . \quad (579)$$

i.e., from (578)

$$\phi + w = \frac{e^2}{Dr} \quad . \quad . \quad . \quad . \quad (580)$$

For the gram molecule, therefore

$$\Phi + W = \frac{Ne^2}{Dr} \quad . \quad . \quad . \quad . \quad (581)$$

¹ A. Neuberger, *Proc. Roy. Soc., A*, **158** (1937), 68.

Now, $W + \Phi$, which is the total electrical work gained by removing a proton from the carboxyl group, is approximately equal to the difference between the free energies of ionisation of the parent acid and the amino-acid—*i.e.*, from (171) and (581), assuming the chain effect Φ to be independent of the solvent

$$\bar{F}_{\text{acid}} - \bar{F}_{\text{amino-acid}} = W + \Phi = RT \ln \frac{K_1}{K_2} \quad (582)$$

and
$$\frac{Ne^2}{D_I r} + \Phi = RT \ln \frac{K_1^I}{K_2^I} \quad (583)$$

$$\frac{Ne^2}{D_{II} r} + \Phi = RT \ln \frac{K_2^{II}}{K_1^{II}} \quad (584)$$

or by subtracting (584) from (583)

$$\frac{Ne^2}{RT r} \left(\frac{1}{D_I} - \frac{1}{D_{II}} \right) = \ln \frac{K_1^I K_2^{II}}{K_1^{II} K_2^I} \quad (585)$$

From equation (585) values for r , the dipole distance, may be calculated, and although many simplifying assumptions have been made in obtaining the equation, the values are of the same order of magnitude as those found independently. They confirm the view that there is no tendency to ring formation in the chains of ω -amino-acids, but that the chain probably has the normal zig-zag structure of ordinary saturated hydrocarbon chains, modified perhaps by a slight curvature due to the large electrostatic attraction between the end-groups. Neuburger's view that the effect of a charged substituent introduced into a carboxylic acid should be divided into a chain and a charge effect is also confirmed by a comparison of the dissociation constants of the ω -amino- and the ω -bromo-acids. If only charge effects were present a rapid rise would be expected in the pK value from amine to amino-acid, whereas the reverse is the case, due to the predominating influence of the chain effect. In the bromo-acids, and also in the amino-esters, the rise in pK due to the charge effect is observed.

Evidence of quite a different character than these electrical measurements for the zwitterionic structures of amino-acids has been supplied¹ from their molecular volumes,

¹ Cohn, McMeekin, Edsall, and Weare, *J. Amer. Soc. Biol. Chem.*, **27** (1933), xxviii.

which are below those calculated for the simple formula $\text{NH}_2\text{R}\cdot\text{COOH}$. This fact appears to show that the solid amino-acids must have a closer packing than the corresponding fatty acids, and this would be compatible with a dipolar structure. The evidence is especially confirmed by the fact that the formyl derivatives of the acids and the hydantoins have molecular volumes corresponding much more closely with the calculated values. On this criterion, however, urea would appear to exist not at all in the zwitterion form, although it increases the dielectric constant of water.

Apart from their unique electrical properties, zwitterion structures should have a strongly marked influence on solubility effects, and powerfully dipole compounds like the amino-acids are, in fact, observed to increase the solubility of other salts in water when they are added to their solutions. Moreover, they are themselves more soluble in aqueous salt solutions than in water. Investigations of the solubility of one zwitterion in a solution of another and an explanation of the relations which are observed should therefore give a preliminary indication of the forces obtaining in the physiological environment.¹ Kirkwood has worked out a generalisation of the Debye-Hückel theory for an arbitrary charge distribution, from which he obtains a relation for the logarithm of the activity coefficient of a zwitterion in the presence of a neutral salt. He finds that this function is "proportional to the ionic strength of the salt, to the square of the dipole moment of the zwitterion, and inversely proportional to the temperature, the dielectric constant, and the sum of the radii of the zwitterion and the salt."² From measurements on the activity of ampholytes in the presence of neutral salts, it is therefore possible to make independent estimates of the dipole distance which, considering the generalised nature of some of the assumptions made in Kirkwood's theory, show remarkable agreement with results from X-ray measurements for the simpler amino-acids so far investigated.³

¹ Cohn, McMeekin, Edsall, and Weare, *J. Amer. Soc. Biol. Chem.* (1931).

² J. Kirkwood, *J. Chem. Phys.*, 2 (1934), 351.

³ E. J. Cohn, *Ann. Rev. Biochem.*, 4 (1935), 100.

The Structures of Proteins.

The fact that proteins almost certainly have a structure built up from amino-acid residues by means of polypeptide linkages¹ (especially as protein-like molecules have been synthesised from amino-acids) suggests that the proteins are themselves zwitterions, at least in their fibrous forms. The simpler polypeptides certainly have a dipolar structure, as is shown by the influence of formaldehyde on their acid and base titration curves (see below). In the globular forms, the structure of which and the relation of which to the fibrous form are not yet completely understood, the state of affairs is probably quite different. It has, however, been shown from X-ray studies that, during the process of denaturation of the globular proteins, there always appear polypeptide chains, which can often be drawn out into artificial fibres.² If, in the globular form of a protein molecule, the charges of the amino- and carboxylic groups are brought sufficiently close together, there will be a marked decrease in the zwitterion properties in this form, due to the small separation of the charges, and consequently a decrease in the dipole moment of the molecule. If, however, denaturation is a process whereby the long, fibre-like form is produced, this should be accompanied by a sharp rise in the intensity of the properties associated with a zwitterion of high moment. In the zwitterion form, for example, the protein molecules should be able to pack into a compact solid structure which would have a lower solubility than the much more open structure of the globular form. The possible change from globular to zwitterion form during denaturation may therefore account for the decreased solubility of the denaturated protein when there is no coagulation during the process.³

Although it has not been possible, as yet, to determine

¹ E. Fischer, *Ber.*, **39** (1906), 530.

Abderhalden (*Z. physikal. Chem.*, **47** (1906), 159) describes feeding experiments which show that polypeptides are degraded in the animal organism exactly like proteins.

² W. T. Astbury and R. Lomas, *J.C.S.* (1935), 846.

W. T. Astbury, S. Dickinson, and K. Bailey, *Biochem. J.*, **29** (1935), 2351. ³ *Ann. Rev. Biochem.*, **1** (1932), 161.

the dipole moments of proteins in solution, observations on denaturated proteins when these are spread in surface layers so that the conditions approximate to the type of arrangement present in the solid state, enable estimates to be made of the moments of proteins in solution. These show that the moment in solution will be very high indeed, and that, therefore, the protein molecules will presumably exist in some charged form, analogous to the zwitterion form of simpler ampholytes.

The Dissociation Constants of Zwitterions.

Bjerrum¹ supposed that, in solution, amphoteric electrolytes (or "ampholytes") underwent an interaction with water similar to that of other acids and bases, the ampholyte existing in solution in the three species, cation $^+\text{NH}_3\text{R}\cdot\text{COOH}$, anion $\text{NH}_2\text{R}\cdot\text{COO}^-$, and zwitterion $^+\text{NH}_3\text{R}\cdot\text{COO}^-$. It will be realised that this is not the same as Bredig and Walker's view,² which stated the fundamental equilibria equations in terms of the species $\text{NH}_2\text{R}\cdot\text{COOH}$ as the undissociated molecule, a hydrated form of this $\text{HONH}_3\text{R}\cdot\text{COOH}$ (from which all the ions could be obtained by splitting off H^+ or OH^-), and the two ions NH_2RCOO^- and $^+\text{NH}_3\text{R}\cdot\text{COOH}$. For the latter ionic species

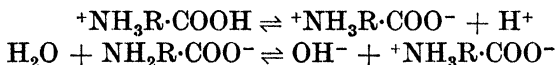
$$\left. \begin{aligned} k_{\text{acid}} &= \frac{(\text{NH}_2\text{R}\cdot\text{COO}^-)(\text{H}^+)}{(\text{NH}_2\text{R}\cdot\text{COOH})} \\ \text{and} \quad k_{\text{base}} &= \frac{(^+\text{NH}_3\text{R}\cdot\text{COOH})(\text{OH}^-)}{(\text{NH}_2\text{R}\cdot\text{COOH})} \end{aligned} \right\} \quad \cdot \quad (586)$$

are the dissociation constants, leaving activity terms substituted in place of concentrations in order to bring the equations more into accord with subsequent formulæ. Although Walker regarded the hydrated form $\text{HO}\cdot\text{NH}_3\text{R}\cdot\text{COOH}$ as strictly an undissociated form, he wrote $(\text{NH}_2\text{R}\cdot\text{COOH})$ in the equilibrium equations, since the ratio $\frac{(\text{NH}_2\text{R}\cdot\text{COOH})}{(\text{HONH}_3\text{R}\cdot\text{COOH})}$ was supposed constant. Bjerrum, however, wrote the dissociation equations in conformity with those for other acids

¹ Bjerrum, *Z. physikal. Chem.* (A), **104** (1923), 147.

² Walker, *Proc. Roy. Soc.*, A, **73** (1906), 155.

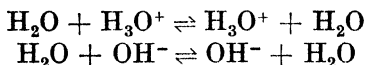
and bases as they were conceived at that time (1923), viz.:



or in terms of the general equations for acid-base dissociation

$$\left. \begin{aligned} \text{H}_2\text{O} + {}^+\text{NH}_3\text{R}\cdot\text{COOH} &\rightleftharpoons {}^+\text{NH}_3\text{R}\cdot\text{COO}^- + \text{H}_3\text{O}^+, \\ K_{\text{acid}} &= \frac{({}^+\text{NH}_3\text{R}\cdot\text{COO}^-)(\text{H}_3\text{O}^+)}{(\text{NH}_3^+\text{R}\cdot\text{COOH})} \\ \text{H}_2\text{O} + \text{NH}_2\text{R}\cdot\text{COO}^- &\rightleftharpoons {}^+\text{NH}_3\text{R}\cdot\text{COO}^- + \text{OH}^-, \\ K_{\text{base}} &= \frac{({}^+\text{NH}_3\text{R}\cdot\text{COO}^-)(\text{OH}^-)}{(\text{NH}_2\text{R}\cdot\text{COO}^-)} \end{aligned} \right\} \quad (587)$$

which show a complete analogy to the acid-base dissociation equations for the ampholyte water,



Since also

$$K_{\text{H}_2\text{O}} = (\text{H}_3\text{O}^+)(\text{OH}^-) \quad . \quad . \quad . \quad (588)$$

it follows from (586) that

$$\left. \begin{aligned} K_{\text{acid}} &= \left(\frac{K_{\text{H}_2\text{O}}}{k_{\text{base}}} \right) \\ K_{\text{base}} &= \left(\frac{K_{\text{H}_2\text{O}}}{k_{\text{acid}}} \right) \end{aligned} \right\} \quad . \quad . \quad . \quad (589)$$

and

It was therefore supposed possible to determine the new dissociation constants from the old constants without having recourse to any new experimental methods. Determinations of the acid and base constants had been made chiefly by hydrolytic methods by observing the influence of the ampholyte on the hydrolysis of methyl acetate, or by conductivity measurements. In the very dilute solutions, however, the low conductivities of amphoteric electrolytes vitiated the results first obtained by this latter method, for the small conductivities could not be measured with sufficient accuracy. Attempts have been made to measure the acid dissociation constants by the conductivity methods applied to ordinary weak acids, but the results obtained are very conflicting and unreliable, and very little work has been carried out on the con-

ductivities of ampholytes. The method has, however, been successfully applied to the determination of the acid ionisation constant of sulphanilic acid,¹ for, since conductivities are additive, their ratios are a measure of the sulphonate ion concentrations at respective total acid concentrations; and if c be the concentration of (H_3O^+) , and therefore of sulphonate ion at a concentration η , and cx that at η_1 , where x is the ratio of the conductivities,

$$\frac{c^2}{\eta - c} = K = \frac{(cx)^2}{\eta_1 - rc} \quad . \quad . \quad . \quad (590)$$

from which K may be found. The old dissociation constants found by these methods for glycine were $k_{\text{acid}} = 1.2 \times 10^{-10}$ and $k_{\text{base}} = 1.9 \times 10^{-12}$ at 17.5°C ,² and using these values Bjerrum finds $pK_{\text{acid}} = 2.73$ and $pK_{\text{base}} = 4.15$.³ These constants are not only the carboxyl and amino-groups' characteristic dissociation constants, but they are identical with the hydrolysis constants corresponding to the old acid and base dissociation constants. Of the more recent methods for determining the effective acid and base dissociation constants, the method of potentiometric titrations is the most important, particularly as it has led to a fundamental revision of the interpretation of the titration curves of ampholytes in terms of the old theories of their structure (see p. 398).

An important consequence of Bjerrum's theory is that instead of the previous two constants k_{acid} and k_{base} given for such amino-acids as asparagine, there are strictly three, two acid dissociation constants which Bjerrum calculated to be pK'_{acid} (first stage) = 1.98, and pK''_{acid} (second stage) = 3.84. Of these two, the former actual dissociation constant is greater than the latter (from the meaning of pK). The explanation of this behaviour will almost certainly follow from the same process as was found

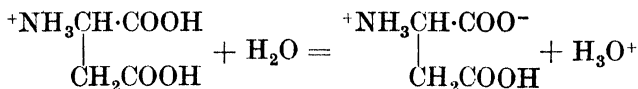
¹ A. E. Stearn, *J. Gen. Physiol.*, **10** (1926-1927), 381.

² Michaelis and Rona, *Biochem. Z.*, **49** (1913), 248.

³ The pK value (dissociation exponent) is defined as follows.

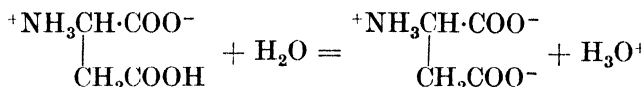
$$\begin{aligned} \text{If} \quad & pK = x \\ & \log_{10} K = -x. \end{aligned}$$

to operate in the ordinary organic dibasic acids. The equilibria in a solution of this particular amino-acid are :



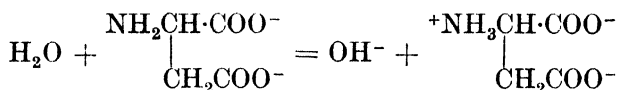
for which
$$K'_{\text{acid}} = \frac{(\text{H}_3\text{O}^+)(+ -)}{(+)}^1 \quad . \quad . \quad (591)$$

The zwitterion may then undergo a further stage of dissociation in accordance with the equation,



for which
$$K''_{\text{acid}} = \frac{(\text{H}_3\text{O}^+)(+ - -)}{(+ -)} \quad . \quad . \quad (592)$$

The ampholyte is therefore able to give two amphoteric ions $+ -$ and $+ - -$. The base dissociation constant is associated with the equilibrium :



the constant being

$$K_{\text{base}} = \frac{(\text{OH}^-)(+ - -)}{(- -)} \quad . \quad . \quad (593)$$

The doubly ionised form involved in the base dissociation equilibrium may be expected to have very high proton attracting properties, and it is hardly surprising, therefore, that dibasic monoamino-acids have a high base dissociation constant. For a similar reason, due to the high proton donating properties of doubly ionised diacid monobasic amino-acids, these have only one, and that a high, acid dissociation constant.

Strictly speaking, the dissociation equations of any ampholyte should have included terms due to the species $\text{NH}_2\text{R}\cdot\text{COOH}$, which might be present as a separate

¹ The notation $(+ -)$ is used to denote the activity of the ion ${}^+\text{NH}_3\text{CH}\cdot\text{COO}^- \begin{array}{c} | \\ \text{CH}_2\cdot\text{COOH} \end{array}$ and similarly expressions are used for the other possible ions.

molecular form in solution. Such equations may be developed by replacing the term for the (totally) uncharged molecules ($^+\text{NH}_3\text{R}\cdot\text{COO}^-$) in (591), (592), and (593) by the term $[(\text{NH}_2\text{R}\cdot\text{COOH}) + (^+\text{NH}_3\text{R}\cdot\text{COO}^-)]$. A direct comparison of the constants thus obtained, with those on the assumptions that no $\text{NH}_2\text{R}\cdot\text{COOH}$ is present, should give an estimate of the extent to which the ampholyte exists in the zwitterion form. In this way it has been shown that the aliphatic amino-acids exist at least to the extent 99.9% in the dipole form, but that aromatic amino-acids appear to show variations in the proportion of zwitterion, from one acid to another. The reason for these variations in the proportions of zwitterion form and uncharged molecules may be attributed to the values of K_{acid} and K_{base} relative to those of an ordinary acid of similar molecular complexity (*e.g.*, acetic acid and glycine) and of ammonia respectively. For if K_{base} and K_{acid} greatly exceed these values there will be very little tendency to hydrolytic dissociation and correspondingly few molecules of the uncharged form. The question to what extent the amino-acid exists in the zwitterion form is obviously one of considerable importance, since the value of the ratio of zwitterionic to normal form will largely determine the physical and chemical properties of the substance.¹

Determination of the Proportion of Zwitterion Form.

Even for some years after Bjerrum's revival of the zwitterion conception of Küster, Walker and Adams, it was not found possible to make an unequivocal experimental determination of the ratio of the zwitterionic to uncharged forms. The method used by Bjerrum was not really satisfactory, and at best could only give a qualitative estimate of the ratio. Ebert² first suggested the possibility of determining the ratio

$$K_v = \frac{(^+\text{NH}_3\text{R}\cdot\text{COO}^-)}{(\text{NH}_2\text{R}\cdot\text{COOH})} \quad . \quad . \quad . \quad (594)$$

from measurements of the dissociation constants of the

¹ Edsall and Blanchard, *J. Amer. Chem. Soc.*, **55** (1933), 2337.

² Ebert, *Z. physikal. Chem.*, **121** (1926).

amino-acid esters. The value of K_1 may be expressed in terms of the equilibria which must exist if both zwitterion and uncharged structures are postulated, but the determination of these individual constants may be facilitated by expressing them in terms of the single constant :

$$K_1 = \frac{(^+\text{H}_3\text{O})(\text{NH}_2\text{R}\cdot\text{COOH})}{(^+\text{NH}_3\text{R}\cdot\text{COOH})} \quad . \quad . \quad (595)$$

In order to find this, however, it must be assumed that the constant K_1 is the same as that for the ester, but since the dipole moment of $\text{R}\cdot\text{COO}\cdot\text{CH}_3$ and $\text{R}\cdot\text{COO}\cdot\text{H}$ are almost identical, the assumption appears justified. A potentiometric titration of the ester will, therefore, give K_1 , and in this way Ebert confirmed Bjerrum's view that the aliphatic amino-acids are present almost exclusively in the dipole modification. The method has been extended¹ by similar observations on the more stable amino-ester hydrochlorides and has shown that all aliphatic amino-acids, even those like leucine with a long hydrocarbon chain, exist almost exclusively as zwitterion, K_1 ranging from 4×10^4 to 1×10^6 , although for aminophenols K_1 was found to be not very far from unity agreeing with Bjerrum's calculation.

The Titration Curves of Zwitterions.

In accordance with the long-established view that ampholytic amino-acids have a structure $\text{NH}_2\text{R}\cdot\text{COOH}$, a titration of this ampholyte with strong acids and strong alkalis should give respectively the base and acid dissociation curves; for, owing to the relatively weak acid and base properties of an ampholyte on the old view, this will behave as a base only towards a strong acid, but will exert almost exclusively its acid function towards a strong base. Dissociation curves of the ampholyte against added acid and base, when plotted on the assumption that the ampholyte has only weak acid and base properties, will have the form shown (Fig. 96). Here the basic-dissociation is supposed complete when the maximum amount of strong acid has been added and vice versa. Titration curves

¹ Edsall and Blanchard, *loc. cit.*

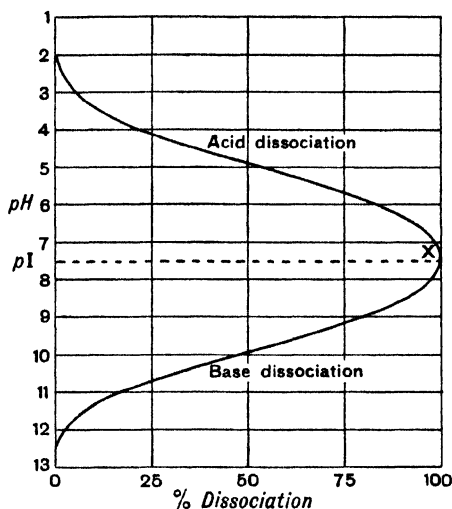


FIG. 96.—DISSOCIATION CURVES FOR AMPHOLYTIC AMINO ACIDS.

following the same general form as those shown in Fig. 96

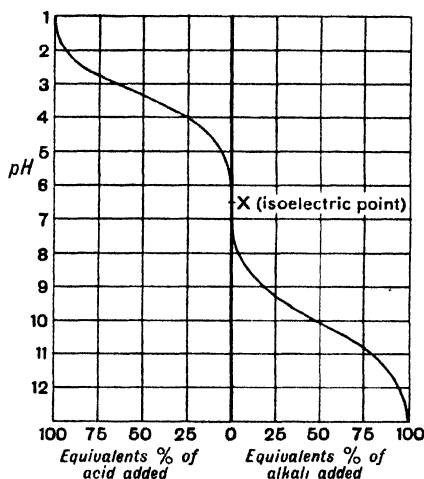


FIG. 97.

have been obtained by measuring the pH potentiometrically as acid or base was added to the ampholyte¹ (Fig. 97).

¹ L. J. Harris and Harris and Birch, *Biochem. J.*, **24** (ii) (1930), 1030. Harris, *Proc. Roy. Soc., B*, **95** (1923), 440, 500; *ibid.*, **B**, **104** (1928-1929), 412.

The view that the amino-acids exist almost exclusively as zwitterions, however, implies that, since the amino-group is already ionised, addition of a strong acid will simply depress the ionisation of the weaker carboxyl group. The addition of, say, hydrochloric acid would therefore measure *not the base, but the acid dissociation constant*, and similarly for the addition of a strong base like caustic soda the dissociation constant observed will be that of the substance behaving in its basic capacity.¹ These results are, of course, the direct reverse of those previously accepted on the view that the undissociated ampholyte molecule was $\text{NH}_2\text{R}\cdot\text{COOH}$. The titration curves (Fig. 97) which are plotted with the two sections of the curve separated on to separate graphs (compare Fig. 96) show complete acid and base dissociation at the isoelectric point X ,² and the base dissociation curve will be that plotted during addition of alkali and the acid curve that during addition of acid. Which curve is the acid dissociation curve and which the base dissociation curve cannot be foretold by inspection, since the entire titration curve has precisely the same appearance in each case, the difference in the allocation of the two portions of the curve depending on whether or not the titrated ampholyte is present as a zwitterion. If, therefore, allocation of the two portions of the curve were possible, a determination of the structure in the 'neutral' state would also immediately be possible, and this process has been accomplished by the 'formal' titration method.

The addition of formaldehyde to an amino-acid to suppress the basic dissociation (on the old view) by methylenation of the amino-group was first employed by Sørensen³ as a means of titrating amino-acids as ordinary organic acids against a strong base: on the zwitterion view, however, addition of formaldehyde will not affect the titration curve of the amino-acid against a strong acid (which on the old

¹ F. L. Hahn and Klochmann, *Z. physikal. Chem.*, **162** (A) (1932), 318.

² Sørensen, *Comp. Rend. Lab. Carls.*, **9** (1912), 121.

³ The isoelectric point is defined as that at which the proportion of ampholyte dissociated as acid is equal to that dissociated as base. The isoelectric exponent pI is the pH value of the solution at the isoelectric point (see p. 406).

view was the base dissociation curve), but it will affect that portion of the curve obtained by titration against strong bases (which represents the true base dissociation curve in the sense of decreased basicity)—i.e., on titration in the presence of increasing quantities of formaldehyde, if the amino-acid is present in the zwitterion form, the base titration curve will be shifted towards the region of lower alkalin-

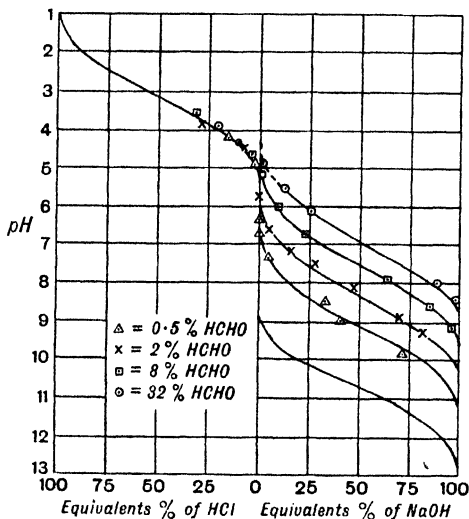


FIG. 98.—FORMAL TITRATION CURVES FOR ZWITTERIONS.

ity and decreasing pH's. The work of Harris¹ completely confirms the zwitterion structure for glycine, alanine, and phenylalanine and a number of other amino-acids in this way, and the curves which were obtained for the base titration of glycine in the presence of 0.5%, 2.8%, and 32% concentrations of formaldehyde are illustrated (Fig. 98). These show quite clearly that the addition of formaldehyde has no effect whatever on the acid curves. The amino-acids, then, far from being able to dissociate only weakly basically and weakly acidically, do really have quite high acid and base dissociation constants compared with the average organic acids, and this is a fact which must always be

¹ Harris, *loc. cit.*, and *Proc. Roy. Soc., B*, 134 (1928-1929), 412-455.

remembered when discussing their ionic equilibria in solutions. By a similar method to the above process of electrometric titration, it has been established that di- and tri-peptides are zwitterionic in structure, since again only the true basic curve—*i.e.*, the caustic soda titration curve—is affected by titration in the presence of formaldehyde, and the results have been extended to the protein gelatin, for which they confirm the independent evidence supplied for this conclusion from solubility measurements. In the case of aminophenols, however, where, as Bjerrum showed, the zwitterion is present only to a small extent, if at all, it is the acid titration curve which is shifted towards the region of greater alkalinity by titration in the presence of formaldehyde, confirming that these are present to a preponderating degree as ordinary uncharged molecules—*e.g.*, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$.

Sørensen's formal titration method has been improved by using alcohol in place of formaldehyde (a modification of Forman's method of titration), together with caustic soda. 85% is employed and alcohol thymolphthalein (which has a more alkaline *pT* and a sharper end-point) is used in place of phenolphthalein as indicator. With this procedure, amino- or imino-groups present in the internal salt structure show no basicity, and the amino-acid may be titrated directly against strong alkali as in the formal method.¹ The formal and alcohol titration methods, however, suppress base dissociation and Linderstrøm-Lang has introduced a method for titration in the presence of 90% acetone² using benzene azonaphthylamine as indicator in which the presence of the acetone suppresses acid dissociation, and therefore influences only the acid titration curve of an amino-acid. Before the importance of the zwitterion conception was realised, this method was assumed therefore to give an estimate of the base groups, although now the reverse view must be held, since acid titration does not affect base dissociation, but only suppresses the acid dissociation. This acetone titration method is found to give fairly

¹ L. J. Harris, *Proc. Roy. Soc., B*, **104** (1928–1929), 412.

² K. Linderstrøm-Lang, *Z. physiol. Chem.*, **173–184** (1928), 32.

accurate results when applied to complicated systems, since, in contrast to the formal and alcohol titration methods, it employs a wide range of pH for titration.¹ In the latter cases the degree of accuracy attainable depends largely on the careful choice of an indicator, but the application of such titration methods to protein hydrolysis experiments must be made only after a careful consideration of whether or not the liberated groups are first neutralised to the chosen indicator.

The Degree of Dissociation Residue and the Isoelectric Point of Ampholytes.

It has frequently been supposed that the titration curves for an ampholyte may be plotted theoretically from a knowledge of the acid and base dissociation constants by means of the Henderson equation (p. 449)

$$pH = pK_{\text{acid}} + \log \frac{1 - \alpha}{\alpha} \quad (596)$$

but this ignores the fact that equation (596) is deduced only for weak electrolytes, whereas ampholytic electrolytes are strong acids and bases compared with the majority of organic substances. A more convenient method for ampholytes, since it allows a ready calculation of the isoelectric point to be made, was introduced by Michaelis, who plotted, not the degree of dissociation against the pH , but the degree of "dissociation residue." This function is the complement of the degree of dissociation, and it represents the ratio of the undissociated to the dissociated electrolyte.² If ρ represents this degree of dissociation residue, then for an amino-acid $^+NH_3R \cdot COO^-$,

$$\begin{aligned} \rho &= \frac{(^+NH_3R \cdot COO^-) - (^+NH_3R \cdot COOH) - (NH_2CH_2COO^-)}{(^+NH_3R \cdot COO^-)} \\ &= \frac{[U]}{[+A^-]} \text{ (say)} \quad (597) \end{aligned}$$

¹ G. M. Richardson, *Proc. Roy. Soc., B*, 115 (1934), 121, where a critical review of titration methods available for amino-acids is given, together with a list of references.

² Michaelis, "Hydrogen Ion Concentration," 1926, trans. Perlzweig, pp. 61 *et seq.*

Michaelis then supposed that the acid and base dissociation constants were given by

$$K'_{\text{acid}} = \frac{[{}^+\text{NH}_3 \cdot \text{R} \cdot \text{COOH}][\text{H}^+]}{[\text{U}]} \quad . \quad . \quad (598)$$

and

$$K'_{\text{base}} = \frac{[\text{NH}_2 \cdot \text{R} \cdot \text{COO}^-][\text{OH}^-]}{[\text{U}]} \quad . \quad . \quad (599)$$

If we replace activities in (597) by concentration terms and eliminate the terms $[{}^+\text{A}^-]$, $[{}^+\text{A}]$, and $[\text{A}^-]$ from (597), (598), and (599) we have :

$$\rho = \frac{1}{1 + \frac{K'_{\text{acid}}}{[\text{H}^+]} + \frac{K'_{\text{base}}[\text{H}^+]}{K_w}} \quad . \quad . \quad (600)$$

The equilibria constants in (598) and (599) are not, however, defined in accordance with the true acid and base equilibria in the ampholyte solution for which the true equilibrium constants are given from (587) as :

$$K_{\text{acid}} = \frac{({}^+\text{NH}_3 \cdot \text{R} \cdot \text{COO}^-)(\text{H}_3\text{O}^+)}{({}^+\text{NH}_3 \cdot \text{R} \cdot \text{COOH})}$$

$$K_{\text{base}} = \frac{({}^+\text{NH}_3 \cdot \text{R} \cdot \text{COO}^-)(\text{OH}^-)}{(\text{NH}_2 \cdot \text{R} \cdot \text{COO}^-)}$$

The true degree of ionisation residue ρ^* will therefore be

$$\rho^* = 1 - \frac{(\text{H}_3\text{O}^+)}{K_{\text{acid}}} - \frac{(\text{OH}^-)}{K_{\text{base}}}$$

$$\text{or} \quad \rho^* = 1 - \frac{(\text{H}_3\text{O}^+)}{K_{\text{acid}}} - \frac{K_w}{(\text{H}_3\text{O}^+)K_{\text{base}}} \quad . \quad (601)$$

in which the dissociation constants have the values ascribed to them by Bjerrum. Obviously, from equation (601), the influence of the acid dissociation is going to be very small when the $p\text{H}$ of the solution is high, for then only the second term will be appreciable compared with unity and, vice versa, for low $p\text{H}$'s the degree of dissociation residue will be largely governed by the base dissociation constant. Since, however, the undissociated ampholyte is assumed to be in the zwitterion form, ρ^* will represent the degree of dissociation residue of the acid and base dissociation of the zwitterion form, and it will be a measure of the extent to

which this form is present at different hydron concentrations. For glycine, Bjerrum gave the new values for K_{acid} and K_{base} as 1.86×10^{-3} and 7.08×10^{-5} respectively, and using these values, the curve for glycine may be plotted as is illustrated in Fig. 99. As plotted, the graph is essentially the combined effect of the two curves

$$\rho^*_{\text{acid}} = 1 - \frac{(\text{H}_3\text{O}^+)}{K_{\text{acid}}} \quad . \quad . \quad . \quad (602)$$

and

$$\rho^*_{\text{base}} = 1 - \frac{K_{\text{H}_2\text{O}}}{(\text{H}_3\text{O}^+)K_{\text{base}}} \quad . \quad . \quad (603)$$

From the fact that the amino-acid exists almost exclusively

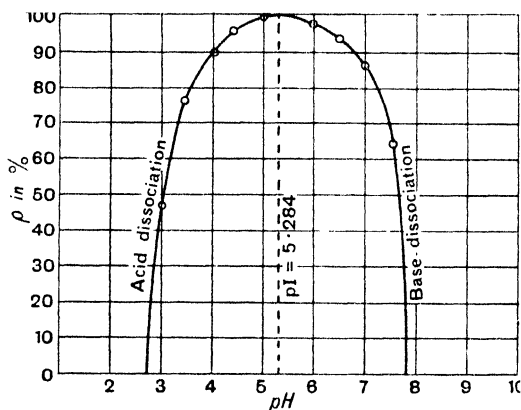


FIG. 99.—DEGREE OF DISSOCIATION RESIDUE OF GLYCINE.

in the dipolar form over a range of pH values, (which for glycine is from about 4.5—6.5), the curve shows clearly that these ampholytes simulate the behaviour of strong acids and bases. At the pH value of 5.284 which will be denoted by pI , the proportion of the substance in the zwitterion form is a maximum, and the quantities of zwitterion present from the dissociated anion and cation are equal. This point has a special significance, since, according to Hardy, it is at this degree of acidity of the surrounding medium that the sign of the charge on an amphoteric colloid particle changes—*e.g.*, on the micelles of the hydrated form of aluminium hydroxide, and for this reason, this characteristic pH of the ampholyte was called by Hardy the “isoelectric point.”

In all ampholytes it corresponds to the point where the ampholyte shows neutrality, and a similar change, as that noticed above in connection with the dissociation, is observed here for many of the properties (*e.g.* charge sign) of colloidal electrolytes. Moreover at the isoelectric point the substance has not only optimum crystallisation, but minimal electrophoresis and osmosis, and these are therefore properties that might be used to determine pI . All these facts correspond with the view that an ampholyte exists at the isoelectric point, to the maximum degree in the true or zwitterion form.

The Isoelectric Point of Ampholytes.

The condition giving the value of the pH at the isoelectric point may be calculated from the expression for the degree of dissociation residue by the same method as that used by Michaelis,¹ but using the corrected equation (601) for ρ^* . For at the isoelectric point, ρ^* is a maximum—*i.e.*, from (601) :

$$\frac{\partial \rho^*}{\partial (H_3O^+)} = -\frac{1}{K_{acid}} + \frac{K_w}{K_{base} (H_3O^+)^2} = 0 \quad . \quad (604)$$

and denoting (H_3O^+) at the isoelectric point by I ,

$$I = \sqrt{\frac{K_{acid}}{K_{base} K_w}} \quad . \quad . \quad . \quad (605)$$

Equation (605) for I gives the same numerical values as Michaelis' expression using the definitions of K_{acid} and K_{base} given in (586), since from (589)

$$\frac{k_{acid}}{k_{base}} = \frac{K_{acid}}{K_{base}}$$

Since all ampholytes do not exist to a preponderating extent in the zwitterion form—*e.g.*, the amino-phenols, the behaviour of which during titration in the presence of formaldehyde suggests that they exist to a large degree in the *nonpolar form*—it might be expected that some effect would be observed on the values of pI when account is taken of possible tautomers. The case has been worked out on the basis of the old acid and base equilibria, and a complicated expression obtained for the hydron concentration at the

¹ Michaelis, *op. cit.*; also Michaelis, *Biochem. Z.*, **33** (1911), 182.

isoelectric point, which included terms involving the concentration ratios of the two tautomers.¹ That the experimental values showed so close an agreement with the simple formula given for pI was attributed to the possibility of the additional terms in the expression for the tautomers having some compensating effects upon each other. If, however, the expression (597) for ρ^* is modified by supposing that the ampholyte $^+A^-$ can also exist in the non-polar form A , the total concentration term of undissociated ampholyte is $(^+A^- + A)$, and this must be substituted wherever $(^+A^-)$ occurred previously—i.e.,

$$\rho^* = 1 - \frac{(A^-) + (A^+)}{(^+A^- + A)} \quad . \quad . \quad . \quad . \quad . \quad (606)$$

$$K_{\text{acid}} = \frac{(^+A^- + A)(H_3O^+)}{(^+A)} \quad . \quad . \quad . \quad . \quad . \quad (607)$$

$$K_{\text{base}} = \frac{(^+A^- + A)(OH^-)}{(A^-)} \quad . \quad . \quad . \quad . \quad . \quad (608)$$

i.e., from (606)

$$\rho^* = 1 - \frac{(H_3O^+)}{K_{\text{acid}}} - \frac{K_w}{K_{\text{base}}(H_3O^+)} \quad . \quad . \quad . \quad . \quad . \quad (609)$$

and

$$I = \sqrt{\frac{K_{\text{acid}}}{K_{\text{base}}}} \cdot K_w \quad . \quad . \quad . \quad . \quad . \quad (610)$$

as before. The postulation of a tautomeric equilibrium between the non-polar and polar forms thus makes no difference to the calculated value of the isoelectric hydron concentration. In the following table (taken from the results quoted by Michaelis) the old and new acid and base dissociation constants are given and some of the values for the isoelectric point, calculated from the above formulae, are worked out.

TABLE XV.
Isoelectric Points of some Ampholytes.

Acid.	k_{base} .	k_{acid} .	$\frac{K_{\text{base}}}{K_{\text{H}_2\text{O}}} = \frac{K_{\text{H}_2\text{O}}}{k_{\text{acid}}}$.	$\frac{K_{\text{acid}}}{K_{\text{H}_2\text{O}}} = \frac{K_{\text{H}_2\text{O}}}{k_{\text{base}}}$.	Observer.	Isoelectric point (calc. from $K_w = 10^{-14}$).
Leucine . . .	2.3×10^{-10}	1.8×10^{-10}	5.5×10^{-4}	4.35×10^{-3}	Winkelblech	8.86×10^{-7}
Glycocoll . .	2.7×10^{-10}	1.8×10^{-10}	5.5×10^{-4}	3.7×10^{-3}	"	8.2×10^{-7}
Phenylalanine	1.3×10^{-10}	2.5×10^{-9}	4×10^{-6}	7.7×10^{-3}	Kanitz	4.4×10^{-3}
Glycylglycine	2.0×10^{-11}	1.8×10^{-8}	5.5×10^{-7}	5.0×10^{-4}	Euler	3.0×10^{-3}
Arsenious acid	1×10^{-14}	6×10^{-10}	1.66×10^{-3}	1.0	Wood	2.4×10^{-3}

¹ Eckweiler, Noyes, and Falk, *J. Gen. Physiol.*, 3 (1921), 219.

Experimental Determinations of the Isoelectric Point.

The method used experimentally for determining the isoelectric point of an ampholyte is governed by the nature of the ampholyte, according as this is easily or sparingly soluble. Most ampholytes, in common with all strong acids and bases, show very little buffer action in the region of the isoelectric point when titrated against strong acids and strong bases, but, like water (for which the isoelectric $pH = pI = 7$), the titration curves show very rapid fluctuations in pH for the addition of small quantities of acid and alkali in the neighbourhood of pI . It is not therefore possible, except in a very limited number of cases—as among the peptides, for instance, where buffer action becomes appreciable—to determine the isoelectric point by titration methods. Michaelis, however, devised two methods by which this could be found,¹ the first for easily soluble ampholytes, depending on the fact that dilute buffer solutions of high buffer value become acidic or basic when acids or bases are added to them. Since ampholytes behave acidically on the lower pH side of the isoelectric point where the acid dissociation



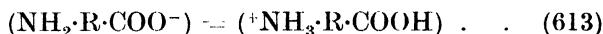
is suppressed by the increased concentration of H_3O^+ , and basically on the higher pH side, the ampholyte will have a strictly neutral reaction only at the isoelectric point. For here, if $(H_3O^+)_I$ denote the hydrion activity and $(OH^-)_I$ the hydroxyl-ion activity at the isoelectric point,

$$\begin{aligned} ({}^+NH_3R \cdot COOH) &= \frac{({}^+NH_3R \cdot COO^-)(H_3O^+)_I}{K_{acid}} \\ &= ({}^+NH_3R \cdot COO^-) \sqrt{\frac{K_w}{K_{base}K_{acid}}} \quad (611) \end{aligned}$$

$$\begin{aligned} (NH_2R \cdot COO^-) &= \frac{({}^+NH_3R \cdot COO^-)(OH^-)_I}{K_{base}} \\ &= ({}^+NH_3R \cdot COO^-) \frac{K_{H_2O}}{(H_3O^+)_I K_{base}} \\ &= ({}^+NH_3R \cdot COO^-) \sqrt{\frac{K_w}{K_{acid}K_{base}}} \quad (612) \end{aligned}$$

¹ Michaelis, *Biochem. Z.*, **47** (1912), 251, or "Hydrogen-ion Concentration," 1926.

i.e., at the isoelectric point



Only at the isoelectric point, therefore, will the ampholyte have no action on a buffer system, and by observing differences in the *pH* of a buffer, the *pH* of which may be varied by the addition of successive known quantities of acid or base, before and after adding the ampholyte, it is possible to determine that *pH* for which there is no change on addition of the ampholyte, and which therefore corresponds to the isoelectric *pH*. An example of this method, quoted by Michaelis, gives *pH* for phenylalanine as 4.57, the calculated value being 4.48. Such a method is, however, not possible for sparingly soluble ampholytes, and Michaelis therefore suggested using for these the principle that the "undissociated" (or more usually the zwitterion form) of an ampholyte is less soluble than the dissociated portion. By adding equal and sufficient amounts of ampholyte to each of a series of hot acetate buffers, the rate of crystallisation can be observed, and the *pH* for which this is a maximum—*i.e.*, where the

TABLE XVI.

Calculated and Experimental Values of the Isoelectric Point.

Acid.	K_{acid} .	K_{base} .	$I_{\text{calculated}}$.	I_{found} .
<i>m</i> -Aminobenzoic acid	8.07×10^{-6}	8.23×10^{-6}	8.8×10^{-5}	6.3×10^{-5}
<i>o</i> -Aminobenzoic acid	4.29×10^{-3}	8.26×10^{-10}	1.7×10^{-4}	1.6×10^{-4}
Aspartic acid . . .	8.33×10^{-3}	6.66×10^{-9}	8.7×10^{-14}	9.3×10^{-14}

solubility of the ampholyte is least, corresponds with the isoelectric point.¹ The results in Table XVI illustrate the degree of agreement to be expected by the method, between the experimental and calculated values.

The agreement between the calculated and experimental values in these acids is quite good considering the qualitative nature of the measurements, and these two experimental methods may be expected to give results with fair accuracy.

¹ Michaelis and H. Davidson, *Biochem. Z.*, **30** (1910), 141.

Systems of Ampholytes in Biology.

During an attempt to imitate the observed behaviour of certain organisms in their staining reactions at varying pH 's by using a number of dyes, particularly acid fuchsin and gentian violet, Stearn showed that the desired effect could be obtained by using a simple mixture of ampholytes.¹ Glycine and sulphonic acid were chosen as the ampholytes, the latter to correspond with the strongly acidic nucleic acid occurring in living matter. The titration curves plotted potentiometrically show a high buffering action around a pH which corresponded to the calculated value of the "isoelectric point of the system"—viz., the point at which the total concentration of the ampholytes present as acidic ions was equal to the total concentration of those dissociated as basic ions. The isoelectric point of the system could be determined by an experimental method similar to that used for simple electrolytes, by observing the conductivities of the mixtures at various pH 's created by the presence of phosphate as buffer. When the difference between the conductivity of the mixture and the sum of the conductivities of the components was a maximum, the properties of the mixture corresponded with the apparent isoelectric point of the system. In general, in any systems of mixed ampholytes the range of pH between the individual isoelectric points of the components is that over which the mutual combination of the ampholytes can take place, and the stability of the system depends on the magnitude of this range. Stearn suggested that it is for this reason that some conjugate proteins—as for example the leithico-proteins—though believed to exist, have not been isolated, whilst others, such as the phospho-proteins and the nucleo-proteins, are easily available.

Proteins themselves are components built out of amino-acid units and, like their parent amino-acids, show amphoteric properties in that they have pH points and zones comparable with those of the simple ampholytes. The importance of these systems of ampholytes is of course

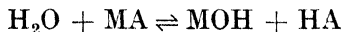
¹ A. E. Stearn, *J. Gen. Physiol.*, 10 (1926-1927), 381, 313, 326, 369.

particularly notable in connection with problems of cell physiology, for mixtures of simple ampholytes may be expected to show something of the behaviour of the more complex mixtures of proteins occurring in living matter, and it may be that the observed phenomena which single observable unit energids (such as the protozoa) show under various imposed conditions of pH and temperature will be explained in terms of the properties of such systems of ampholytes.

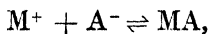
CHAPTER XIII

THE HYDROLYSIS OF SALTS ¹

JUST as the combination of an acid and a base will give a salt and water so the hydrolysis of a salt takes place by the reversal of this reaction



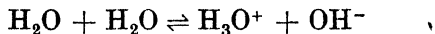
It is obviously necessary, if this process is to be examined quantitatively, to be able to determine the position of the equilibrium—*i.e.*, the extent to which dissociation takes place. When both the acid and the base are “strong” or largely dissociated, the essential reaction, which is



will be able to take place to a large extent, and the salt formed will, in consequence, be only very slightly hydrolysed. If either the acid or the base is a weak electrolyte, the presence of hydrions from the water will set up an equilibrium with the appropriate ions from the salt (which, according both to the Arrhenius dissociation theory and to modern theories, is completely dissociated in aqueous solution). This equilibrium will be far over on the side of undissociated acid or base. In the case, therefore, of a salt of a weak base and a strong acid, of a strong base and a weak acid, or of a weak acid and a weak base, hydrolysis will be considerable in aqueous solution.

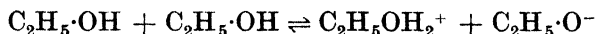
The Hydrolytic Constant of Water.

Water itself undergoes hydrolysis by itself in accordance with the equilibrium

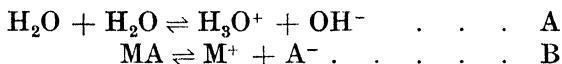


¹ An account of hydrolysis with a table of degrees of hydrolysis is given in Bjerrum's “Die Theorie der Alkalimetrischen und Azidimetrischen Titrierungen,” (1914), pp. 11–15.

a reaction analogous to this taking place also in non-aqueous solvents—*e.g.* :



where the positive ion is quite different from that in water. In an aqueous solution of a hydrolysable salt, the extent to which hydrolysis takes place will be determined by the extent to which the two equilibria :



react upon each other. It is therefore necessary in all cases of hydrolysis in aqueous solutions to know the extent to which the former of the two reversible reactions *A* and *B* takes place. The conductivity of pure water is known from Kohlrausch and Heydweiller's experiments to be very small ¹ (see p. 74), and the law of mass action may be applied to the equilibrium, the water being treated as an electrolyte—*i.e.* :

$$K = \frac{(\text{H}_3\text{O}^+)(\text{OH}^-)}{(\text{H}_2\text{O})(\text{H}_2\text{O})} \quad . \quad . \quad . \quad . \quad . \quad (613)$$

$$\text{and} \quad K_{\text{dis}} = \frac{(\text{H}_3\text{O}^+)(\text{OH}^-)}{(\text{H}_2\text{O})} = \frac{K_w}{55\cdot51} \quad . \quad . \quad (614)$$

But since the concentration of water remains essentially constant at 55·51N, the product

$$(\text{H}_3\text{O}^+)(\text{OH}^-) = K_w \quad . \quad . \quad . \quad . \quad (615)$$

is also constant at a given temperature; K_w is the so-called ionic product of water.

Experimental Determinations of K_w .

Accurate estimates of K_w were first made by Kohlrausch and Heydweiller (see p. 74) from their measurements on the conductivity of the purest water obtainable. The specific conductivity of samples of this water freshly distilled *in vacuo* into platinum vessels, was found to be $0\cdot04 \times 10^{-6}$ reciprocal ohms at 18° C. By Kohlrausch's law of the independence of ionic mobilities, this quantity is equal to the sum of the

¹ Kohlrausch and Heydweiller, *Wied. Annalen.*, 53 (1894), 209; *Z. physikal. Chem.*, 14 (1894), 326.

products of the number of gram ions per c.c. and the limiting mobilities for the ions H_3O^+ and OH^- :

$$0.04 \times 10^{-6} = n[(\lambda_{\text{H}_3\text{O}^+})_{\infty} + (\lambda_{\text{OH}^-})_{\infty}] = n(350 + 174) \quad (616)$$

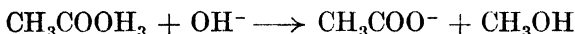
$$\text{i.e., } n = \frac{0.04 \times 10^{-6}}{524} = 0.73 \times 10^{-10} \text{ gram-ions per c.c.} \quad (617)$$

or $n = 0.73 \times 10^{-7}$ gram-ions per litre

Their value for the ionic product of water using the newer values of $(\lambda_{\text{H}_3\text{O}^+})_{\infty}$ and $(\lambda_{\text{OH}^-})_{\infty}$ was, therefore,

$$K_w = n^2 = 0.51 \times 10^{-14} \quad (618)$$

Another method which has been used to determine the ionic product of water depends on the saponification of methyl acetate in water for, in the reaction



for every equivalent of OH^- disappearing, one equivalent of H_3O^+ must be found. The acetic acid which is formed in the first stages of the reaction due to the equivalent formation of H_3O^+ ions may be considered as completely dissociated. Neglecting solvent and salt effects, the catalytic effect of the OH^- ions is found to be about 1400 times that of the H_3O^+ ions. The rate of decomposition of the ester will therefore decrease with time, due to the disappearance of the OH^- ions, until a minimum value of the rate of decomposition is reached where the decreased effect of the OH^- ions is just balanced by the catalytic effect of the now large concentration of H_3O^+ ions. Thus :

$$-\frac{\partial[\text{CH}_3\text{COOCH}_3]}{\partial t} = K_1[\text{OH}^-] + K_2[\text{H}_3\text{O}^+] \quad (619)$$

K_1 and K_2 being the appropriate velocity constants for the catalytic effect of the OH^- ions alone and of the H_3O^+ ions alone respectively. At the minimum we have from (619) :

$$-\frac{\partial}{\partial t} \left[\frac{\partial[\text{CH}_3\text{COOCH}_3]}{\partial t} \right] = K_1 \frac{\partial[\text{OH}^-]}{\partial t} + k_2 \frac{\partial[\text{H}_3\text{O}^+]}{\partial t} = 0 \quad (620)$$

and since

$$[\text{OH}^-][\text{H}_3\text{O}^+] = K_w \quad (621)$$

by differentiating we obtain :

$$[\text{H}_3\text{O}^+] \frac{\partial[\text{OH}^-]}{\partial t} + [\text{OH}^-] \frac{\partial[\text{H}_3\text{O}^+]}{\partial t} = 0 \quad . \quad (622)$$

In order that (620) and (622) shall hold simultaneously :

$$\frac{[\text{H}_3\text{O}^+]}{[\text{OH}^-]} = \frac{K_1}{K_2} = 1400 \quad . \quad . \quad (623)$$

The conductivity of aqueous solutions of methyl acetate will be almost entirely due to the acetic acid, so that the minimum rate of reaction may be determined from the rate of change of conductivity. The amount of acetic acid may be found by titration against standard baryta, giving the value of (H_3O^+) . The value of (OH^-) is 1400 times less, and the ionic product for water may then be calculated, one of the values so obtained ¹ being

$$K_w = 1.96 \times 10^{-14} \quad . \quad . \quad . \quad (624)$$

As mentioned above, however, this takes no account of salt effects due to the acetic acid and the acetate ions, and in order to correct for these two effects, Dawson calculated the dissociation constant of water from the more accurate equation ² (for ethyl acetate) :

$$-\frac{\partial[\text{CH}_3\text{COOC}_2\text{H}_5]}{\partial t} = K_{\text{OH}^-} [\text{OH}^-] + K_{\text{H}_3\text{O}^+} [\text{H}_3\text{O}^+] \\ + K_{\text{A}^-} [\text{CH}_3\text{COO}^-] + K_{\text{HA}} [\text{CH}_3\text{COOH}] \quad (625)$$

i.e., from (621)

$$-\frac{\partial[\text{CH}_3\text{COOC}_2\text{H}_5]}{\partial t} = K_{\text{OH}^-} \frac{K_w}{[\text{H}_3\text{O}^+]} + K_{\text{H}_3\text{O}^+} [\text{H}_3\text{O}^+] \\ + K_{\text{A}^-} [\text{CH}_3\text{COO}^-] + K_{\text{HA}} [\text{CH}_3\text{COOH}] \quad (626)$$

Systematic experiments on the hydrolysis of ethyl acetate under the catalytic influence of N/10 acetic acid together with $x\text{N}$ sodium acetate then gave K_{A^-} and K_{HA} and the values for K_{OH^-} and $K_{\text{H}_3\text{O}^+}$ were obtained by assuming that in strongly alkaline and acid solutions, one or other of the terms became negligible. The minimum velocity rate was found by experiments with buffer solutions of varying but

¹ J. J. A. Wijs, *Z. physikal. Chem.*, **11**, 492.

² Dawson, *J.C.S.* (1927), 1290.

known pH , and K_w at 25° C. was found to have the value

$$K_w = 1.25 \times 10^{-14} (627)$$

Measurements of the rate of hydrolysis of ethyl acetate in acetate buffers by Karlsson, carried out in quartz tubes at 85° C., give $K_w = 34 \times 10^{-14}$, comparing with 44×10^{-14} by E.M.F. and 28×10^{-14} by hydrolysis experiments at the same temperature.¹

Hudson has determined K_w by a similar method to that based upon the rates of hydrolysis of esters, by following polarimetrically the mutarotation of glucose in aqueous

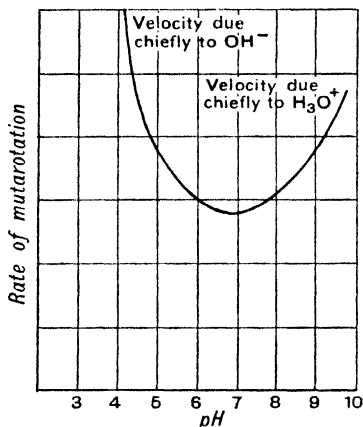


FIG. 100.—VARIATION OF RATE OF MUTAROTATION WITH pH .

solutions.² In acid solutions of known pH , obtained by using buffers of acetic acid and sodium acetate which have the same pH at different concentrations, the velocity was found to be represented by the equation :

$$\text{velocity} = V_{\text{spontaneous}} + \frac{K_2[H_3O^+]}{K_4[CH_3COOH]} + \frac{K_3[OH^-]}{K_5[CH_3COO^-]} \quad (628)$$

where the last two terms represent salt effects, $K_4[CH_3COOH]$ being approximately proportional to the dissociation constant of acetic acid, and $K_5[CH_3COO^-]$ inversely proportional to this. Hudson, however, neglected the salt effect, and so obtained erroneous values of K_2 and K_3 . The hydron and hydroxyl ion effects were, however, easily separated by a suitable adjustment of the pH values of the solution, and

¹ Karlsson, *Z. anorg. Chem.*, **119** (1921), 19.

² Hudson and Dale, *J. Amer. Chem. Soc.*, **39** (1917), 320.

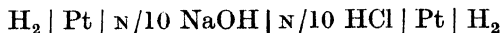
K_2 and K_3 could then be calculated. The spontaneous velocity of reaction could also be determined by plotting the observed velocity of reaction against the pH values of the solution and observing the velocities when $pH = 7$. The velocity at this point will be composed of the spontaneous velocity and the velocity terms due to salt effects which are known, so that the spontaneous velocity may be calculated. If, now, the velocity of the mutarotation V_0 is observed in pure water, since :

$$(H_3O^+) = (OH^-) \\ V_0 = [H_3O^+][K_2 + K_3] + V_{\text{spontaneous}} \quad (629)$$

$$\text{i.e., } [H_3O^+] = \sqrt{K_w} = \frac{V_0 - V_{\text{spontaneous}}}{K_2 + K_3} \quad (630)$$

and the accuracy of the method depends only on the accuracy with which $(V_0 - V_{\text{spontaneous}})$ may be determined. Brönsted has shown that it is more convenient and more accurate to measure the rates of mutarotation by dilatometer methods rather than polarimetrically, provided very great care is taken to ensure accurate temperature control.¹

E.M.F. measurements applied to a determination of K_w have the advantage, however, over these methods, of being independent of any specific theories of catalysis in solution, and the method employed is similar to that used for determining degrees of hydrolysis. The E.M.F. at 25° C. of the cell :



is 0.6928 volt. The activity of hydrions in the solution of hydrochloric acid and of hydroxyl ions in the caustic soda are found to be 0.0924 and 0.0847 respectively, from the known activity coefficients at these concentrations. If, therefore, a_H represents the activity of hydrions in the caustic soda, equation (371) gives us :

$$E = 0.6928 = \frac{RT}{F} \ln \frac{0.0924}{a_H} = 0.059 \log_{10} \frac{0.0924}{a_H} \quad (631)$$

$$\text{i.e., } \log_{10} \frac{0.0924}{a_H} = 11.7424 \quad (632)$$

$$\text{or } a_H = 0.1672 \times 10^{-12} \quad (633)$$

$$\text{i.e., } K_w = a_H a_{OH} = 0.1672 \times 8.47 \times 10^{-14} \\ = 1.417 \times 10^{-14} \quad (634)$$

¹ Brönsted and Guggenheim, *J. Amer. Chem. Soc.*, **49** (1927), 2554.

This is probably one of the most accurate values for the ionic product of water that is available. Accurate measurements of the degree of dissociation of water by Michaelis, using the E.M.F. method, showed that K_w varies from 0.63×10^{-14} to 3.80×10^{-14} between 16°C. and 40°C. , the values 0.93, 1.01, and 1.10 respectively being given at 21° , 22° and 23°C.

The Hydrolysis of Salts.

The three cases of hydrolysable salts already enumerated will now be treated separately :

(a) The Salt of a Weak Acid and a Strong Base or of a Strong Acid and a Weak Base.¹

These two types of salts are exactly similar in their behaviour and they will therefore be considered as one type only. When the solutions are sufficiently dilute in the absence of other ions which might have some effect on the activities, the activity of each component may, to a first approximation, be equated to the concentration term. Now the hydrolysis of the salt of a strong base and a weak acid will produce equal quantities of the acid and base, but as only the latter dissociates, there will be, in the solution, an excess of hydroxyl ions, and the solution therefore shows an alkaline reaction (*e.g.*, potassium cyanide in water). The degree of hydrolysis is defined by :

$$\alpha = \frac{[\text{OH}^-]}{[\text{salt}]} \quad . \quad . \quad . \quad . \quad . \quad (635)$$

where the term [salt] denotes the total concentration of the salt. Since during hydrolysis as much acid is produced as base, and only the base is completely dissociated, we may write :

$$[\text{MOH}] = [\text{OH}^-] \quad . \quad . \quad . \quad . \quad (636)$$

$$[\text{OH}^-] = [\text{H}_3\text{O}^+] + [\text{HA}] \quad . \quad . \quad . \quad (637)$$

The dissociation of the acid is expressed by the equation :

$$\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = K_{\text{acid}} \quad . \quad . \quad . \quad . \quad (638)$$

¹ Niels Bjerrum gives the following method for calculating the degree of hydrolysis in his book "Die Theorie der alkalimetrischen und azidimetrischen Titrierungen," (1914).

and the total concentration of the salt is given by

$$[\text{Salt}] = [\text{HA}] + [\text{A}^-] \quad . \quad . \quad . \quad (639)$$

Simultaneously the water equilibrium gives from equation (615) expressed in concentration terms

$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] \quad . \quad . \quad . \quad (640)$$

The last four equations may be solved for each of the four unknowns $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, $[\text{A}^-]$, $[\text{HA}]$, and thus α may be calculated when $[\text{OH}^-]$ is known. The expression obtained is very complicated, but there are three special cases of particular importance. When there is very little hydrolysis, so that α is less than 1% and $[\text{OH}^-] = 10^{-6}$, the concentration of acid $[\text{HA}]$ in (639) is negligible compared with the term $[\text{A}^-]$ —i.e.

$$[\text{Salt}] \simeq [\text{A}^-] \quad . \quad . \quad . \quad (641)$$

and since :

$$[\text{OH}^-] = \frac{K_w}{[\text{OH}^-]} + \frac{K_w[\text{A}^-]}{K_{\text{acid}}[\text{OH}^-]} \quad . \quad . \quad (642)$$

$$\text{then} \quad [\text{OH}^-]^2 = [\text{Salt}] \frac{K_w}{K_{\text{acid}}} + K_w \quad . \quad . \quad . \quad (643)$$

so that :

$$\alpha = \sqrt{\frac{1}{[\text{Salt}] \frac{K_w}{K_{\text{acid}}}} \left(1 + \frac{K_{\text{acid}}}{[\text{Salt}]} \right)} \quad (\text{weak hydrolysis}) \quad (644)$$

If hydrolysis takes place to a moderate extent, so that α is still less than 1% but (OH^-) is greater than 10^{-6} , the total concentration of salt still remains approximately equal to (A^-) but (H_3O^+) may be neglected in (637) :

i.e., (643) will now be

$$[\text{OH}^-]^2 = [\text{Salt}] \frac{K_w}{K_{\text{acid}}} \quad . \quad . \quad . \quad (645)$$

$$\text{and} \quad \alpha = \sqrt{\frac{1}{[\text{Salt}] \frac{K_w}{K_{\text{acid}}}}} \quad (\text{moderate hydrolysis}) \quad (646)$$

When, however, α is greater than 1% and $[\text{OH}^-]$ is greater than 10^{-6} , the approximation of (637) made in (645) for

moderate hydrolysis holds, but no approximation may be made of (639)—*i.e.*

$$[\text{OH}^-]^2 = [\text{Salt}] \frac{K_w}{K_{\text{acid}}} - [\text{OH}^-] \frac{K_w}{K_{\text{acid}}} \quad (647)$$

and

$$\alpha = \frac{\sqrt{\frac{1}{[\text{Salt}] K_{\text{acid}}} \frac{K_w}{K_{\text{acid}}}}}{\sqrt{1 + \frac{K_w}{[\text{Salt}] K_{\text{acid}}}} + \sqrt{\frac{K_w}{[\text{Salt}] K_{\text{acid}}}}} \quad (\text{strong hydrolysis}) \quad (648)$$

The equations are rather more complicated if account is taken of the true degrees of dissociation of the salt and base, α_1^* and α_2^* , for then, in the case, for example, of moderate hydrolysis, equation (645) for $[\text{OH}^-]^2$ becomes :

$$[\text{OH}^-]^2 = [\text{Salt}] \frac{K_w}{K_{\text{acid}}} \alpha_1^* \alpha_2^* \quad (649)$$

$$\text{and} \quad \alpha = \frac{[\text{OH}^-]}{\alpha_2^* [\text{Salt}]} = \sqrt{\frac{\frac{K_w}{\alpha_1^*}}{[\text{Salt}] K_{\text{acid}} \alpha_2^*}} \quad (650)$$

which reduces to the simpler expression when the degrees of dissociation of the acid and base are equal.

It follows from equation (644) for weak hydrolysis, that under these conditions the degree of hydrolysis is proportional to the square root of the concentration. Exactly similar expressions hold for the degrees of hydrolysis of a salt of a strong acid and a weak base, except that here :

$$\alpha = \frac{[\text{H}_3\text{O}^+]}{[\text{Salt}]} \quad (651)$$

or, more accurately :

$$\alpha = \frac{[\text{H}_3\text{O}^+]}{\alpha_2^* [\text{Salt}]} \quad (652)$$

and the expressions previously obtained have $[\text{OH}^-]$ replaced by $[\text{H}_3\text{O}^+]$ and K_{acid} replaced by K_{base} , since only the acid now undergoes practically complete dissociation.

(b) Salt of a Weak Acid and a Weak Base.

For the salt of a weak acid and a weak base, neither the acid nor the base to which it gives rise is completely dissociated, and the solution remains nearly neutral, for dissocia-

tion is only slight, and the dissociation constants are nearly equal. For this case, we have :

$$\alpha = \frac{[\text{OH}^-] + [\text{H}_3\text{O}^+]}{[\text{Salt}]} \quad . \quad . \quad . \quad (653)$$

instead of (635), and equation (636) becomes :

$$[\text{MOH}] + [\text{OH}^-] = [\text{HA}] + [\text{A}^-] \quad . \quad (654)$$

since the amounts of acid and base produced are equal. For the acid and base dissociation constants we may write :

$$\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = K_{\text{acid}} \quad . \quad . \quad . \quad (655)$$

$$\frac{[\text{M}^+][\text{A}^-]}{[\text{Salt}]} = K_{\text{base}} \quad . \quad . \quad . \quad (656)$$

where $[\text{Salt}] = [\text{HA}] + [\text{A}^-] + [\text{MOH}] + [\text{M}^+] \quad (657)$

From (615) $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$

Also in the case of very small hydrolysis the quantities $[\text{MOH}]$ and $[\text{HA}]$ in the expression for the total concentration $[\text{salt}]$ of the salt may be neglected

i.e., $[\text{Salt}] = [\text{A}^-] + [\text{M}^+] \quad . \quad . \quad . \quad (658)$

The solution of these equations then gives :

$$\alpha = \sqrt{\frac{K_w}{K_{\text{acid}} K_{\text{base}}}} \quad . \quad . \quad . \quad (659)$$

so that for small hydrolysis the degree of hydrolysis is independent of the concentration. A simple demonstration of this may be carried out as follows. A neutral solution of methyl orange (which is the salt of a weak acid and a weak base) is treated with first a few drops, then a large quantity of a solution of aniline acetate. In each case the tint produced is the same, showing that the hydrogen ion concentration, and therefore the degree of hydrolysis, has remained the same.¹

Experimental Determinations of the Degree of Hydrolysis.

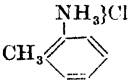
The theoretical rigour of many of the methods which have been employed for the experimental determination of the

¹ H. Tizard, *J.C.S.* (1910), 2490.

degrees of hydrolysis ¹ has been invalidated to a large extent by more recent work. For example, the catalysis of reactions in solution, like the mutarotation of glucose and the saponification of esters (reactions which have from time to time been used to determine the degree of hydrolysis), has been shown to be of a much more complicated nature than was at first supposed. Considering, for example, the method using the saponification of esters ²; this reaction will take place in the presence of hydrolysable salts which give rise to acid or alkali. The velocity of the reaction was considered to be always proportional to the amount of acid added, and it was supposed possible, therefore, to calculate the amount of acid

TABLE XVII.

Degrees of Hydrolysis of Anilinium Salts.

Substance (in n/10 solution).	 NH_3^+Cl	 $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_3^+\text{Cl}$	 $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_3^+\text{Cl}$
Degree of hydrolysis by conductivity	1.5	0.9	1.8
Degree of hydrolysis by inversion of cane sugar	2.6	1.7	3.2

produced from a salt by hydrolysis, by observing its effect on the velocity of reaction. In the case of a salt which hydrolyses to give free alkali, a similar catalysis takes place, but the alkali is used up as the reaction proceeds, and this complicating factor must be allowed for. Even at the time when these methods were employed it was realised that there were many facts known which were unexplained, such as the saponification of esters under the influence of neutral salts, but the catalytic method was nevertheless claimed to give a fairly accurate estimate of the degree of hydrolysis. These methods, however, have been abandoned in favour of determinations based only upon the measurements of physical properties of the solution which are independent of any specific theory of solution. As an example of the variations

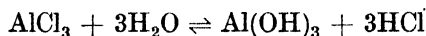
¹ R. C. Farmer, *British Association Report*, 1901, p. 240.

² J. Walker, *Z. physikal. Chem.*, 4 (1889), 319.
Shields, *ibid.*, 12 (1893), 167.

which were at one time observed between measurements from catalysis data, the following table, taken from the results of Farmer is quoted.¹

It is interesting, when surveying these results, to recall that, owing to the impossibility of determining the conductivity to within more than 1%, more importance was attached to the results from the catalytic data than to those from simple physical measurements.

The total number of particles present in a solution is, according to van 't Hoff, directly responsible for the lowering of the freezing point (see p. 12 *et seq.*). On hydrolysis there is always an increase in the number of particles in solution, which results in a difference between the observed lowering of the freezing point and the value calculated on the assumption that there is no hydrolysis. The extent to which the observed and calculated values differ is therefore a direct measure of the degree of hydrolysis. If one of the products of hydrolysis be ionised, account must of course be taken of this, and in the case of a salt of a strong acid and a weak base—*e.g.*



the acid may be considered as completely ionised, the same applying to the strong base produced by the hydrolysis of the salt of a weak acid and a strong base.

A special case of the general method of determining the degree of hydrolysis from estimates of the number of particles in the solution of the hydrolysed salt, utilises the partition coefficient. Thus in the hydrolysis of aniline hydrochloride, according to the equation :



the aniline present at equilibrium may be partitioned between water and benzene, the ratio of the concentrations in the two phases being given by the mass law.² The amount of aniline in the benzene phase may be determined directly by titration, and the total amount of aniline at equilibrium obtained. Knowing, therefore, the initial quantity of aniline hydrochloride in the solution of known strength, the degree of

¹ Farmer, *loc. cit.*

² R. C. Farmer, *J.C.S.*, 79 (1901), 186; *ibid.*, 85 (1904), 1, 714.

hydrolysis at this concentration may be obtained. The results from using this method are not good, however, since there is considerable difficulty in carrying out an accurate quantitative estimation of small quantities of aniline by titration methods. A better procedure consists in shaking a known amount of an $N/10$ solution of hydrogen chloride with a known volume of benzene to which has been added an equivalent amount of aniline. The amount of aniline remaining in the benzene may then be determined by precipitating it with dry hydrogen chloride, evaporating off the benzene, and weighing the aniline hydrochloride. The partition experiment has, of course, to be carried out in a thermostatic vessel, and a small correction, for the volume of benzene taken, may be made to allow for evaporation during the partition experiment. The results given in Table XVIII were obtained by Farmer¹ employing this method for aniline and the toluidines, using in each case 1000 c.c.s of hydrochloric acid and 60 c.c.s of benzene. The partition was carried out at 25° C. and it was necessary to correct this volume for evaporation.

The electrical conductivity is another physical property which may be used to advantage for estimating degrees of hydrolysis in salt solutions. The method depends on the fact that in water the ions, say of anilinium chloride—viz., $C_6H_5NH_3^+$ and Cl^- —are replaced by H_3O^+ and Cl^- , so that in solution the aniline produced will not contribute towards the molecular conductivity. The anilinium ion does, however, affect the conductivity, and its influence must be eliminated. If χ_1 be the molecular conductivity which the unhydrolysed anilinium chloride, $\phi NH_3\}Cl$ would have had, χ_{HCl} that of hydrochloric acid and α the degree of hydrolysis (as a fraction) then :

$$\chi = \text{molecular conductivity observed} = (1 - \alpha)\chi_1 + \alpha\chi_{HCl}$$

$$\text{i.e.} \quad \alpha = \frac{\chi - \chi_1}{\chi_{HCl} - \chi} \quad . \quad . \quad . \quad . \quad (660)$$

Although there is no difficulty in measuring χ_{HCl} and χ_1 , great difficulty has been encountered in attempting to measure the conductivity of aniline hydrochloride when no

¹ R. C. Farmer, *loc. cit.* (1904).

TABLE XVIII.
Degrees of Hydrolysis of Anilinium salts, by Partition Experiments (Farmer).

Substance :							
Partition coefficient .	10.1	13.1	19.1	24.1	—	—	—
Dilution (litres) .	10.0	9.9	32.0	10.0	32.0	32.1	32.0
Concentration of acid taken	0.09969	0.1009	0.1002	0.03130	0.09958	0.03120	0.03132
Concentration of base taken	1.09969	0.1009	0.1002	0.03130	0.09958	0.03120	0.03132
Wt. of hydrochloride from 50 c.c. benzene solution	0.0806	0.2741	0.1783	0.1080	0.1133	0.1106	0.0768
Concentration of free base in water (calc.)	0.00123	0.00255	0.00131	0.000738	0.000655	0.00169	0.000444
Per cent. hydrolysis .	1.56	3.80	1.92	3.69	1.02	3.70	2.22

hydrolysis takes place. Walker adopted a method of analogy by comparing the conductivities at the same dilution of salt, known not to be hydrolysed, with those of the hydrolysed salts, assuming that at equal dilutions the conductivities were the same.¹ This gave a fair estimate when the degree of hydrolysis was large, but for small degrees of hydrolysis, such as occur with aniline and its derivatives, Bredig's method by adding an excess of the free base (which he assumed would not affect the conductivity), sufficient to repress hydrolysis, and taking the molecular conductivity measured under these conditions as equal to χ_1 is less arbitrary. Bredig's measurements² on the hydrochlorides of aniline and toluidine gave the degrees of hydrolysis at a dilution of 32 litres as 2.63% and 3.07%, respectively. Unfortunately, the method is not unequivocal, for quite generally the effects of adding substances, whatever their nature, to solutions of electrolytes are considerable, owing to the changes produced in the ionic strength of the solution and the viscosity and dielectric constant of the medium. Essentially, however, the conductivity method is similar to the partition and freezing-point methods, since it attempts to determine the concentration of the ionised fraction, whereas the partition method estimates the concentration of the unionised fraction, and the freezing-point method determines the total number of extra particles due to hydrolysis.

One unequivocal method has been devised by Denham³ for measuring the degrees of hydrolysis of salts, but it is limited in its application, since it cannot be applied to any salt containing an easily reduced ion (*e.g.*, Fe^{+++} or ClO_3^-), and it is only applicable to the salts of metals the electrode potentials of which are positive on the hydrogen scale. These considerations, however, do not militate against its value as a method of wide application, and it is particularly valuable for determining the degrees of hydrolysis at very low concentrations where all other methods fail. (For a single-stage hydrolysis, such as aniline hydrochloride under-

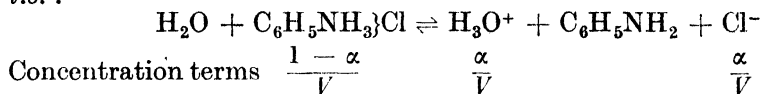
¹ Walker, *Z. physikal. Chem.*, **4** (1889), 333.

Bredig, *ibid.*, **13** (1894), 321.

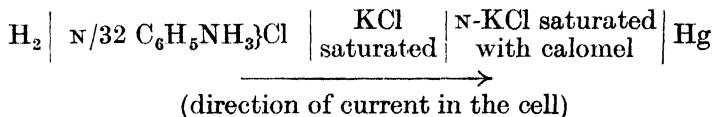
² *Idem*, *ibid.*, **13** (1894), 322.

³ Denham, *J.C.S.*, **93** (1908), 41.

goes, if the degree of hydrolysis at the dilution V is α , the concentrations at equilibrium are, for the anilinium hydrochloride, $1 - \alpha/V$, for the H_3O^+ and Cl^- ions, α/V each, while for the water the concentration is sensibly constant, *i.e.* :



It is assumed that the hydrochloric acid is completely dissociated so that no term for this enters the equation. In this equation V is known, and α/V is the concentration of hydron at equilibrium which may be measured accurately in a suitable cell. Thus if a hydrogen electrode dipping into a solution of aniline hydrochloride of known strength is connected through a suitable liquid bridge (*e.g.*, saturated KCl) with a normal or $N/10$ calomel electrode, and the E.M.F. measured at 25°C . while the cell is kept in a thermostat, the concentration of hydron may be found, and so the degree of hydrolysis calculated at the measured temperature and dilution. The following measurements are taken from Denham's data for the cell :



The E.M.F. of the cell was found to be 0.4655 volt—then, since

$$\frac{RT}{F} \ln [\text{H}_3\text{O}^+] = E - E^0 \quad . \quad . \quad . \quad (661)$$

where E^0 is the potential of a solution normal in respect of H_3O^+ ions, then, taking the absolute potential of the calomel electrode as 0.56 volt, the E.M.F. E^0 is 0.277 volt—*i.e.* :

$$E = 0.56 - 0.4655 = 0.0945 \text{ volt} \quad . \quad (662)$$

or

$$\frac{RT}{F} \ln [\text{H}_3\text{O}^+] = 0.0945 - 0.277 = -0.1825 \text{ volt} \quad (663)$$

This gives, after substituting for the constants R , T , and F ,

$$[\text{H}_3\text{O}^+] = 0.000807 \quad . \quad . \quad . \quad (664)$$

Complete hydrolysis at a dilution of $N/32$ would produce a concentration of hydron $N/32 = 1/32$, assuming complete dissociation of the hydrochloric acid, and therefore under the experimental conditions the percentage hydrolysis is 2.58%. In deducing the concentration of the hydron during hydrolysis, a simplifying assumption has been made—viz., that the acid component of the salt is completely dissociated in the solutions considered. In general, this will not be true, but if the true dissociation constants are known

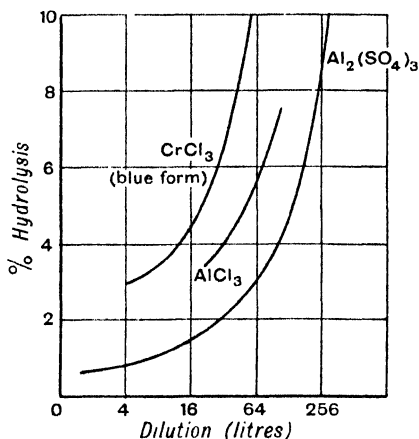
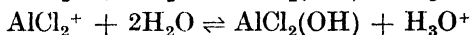
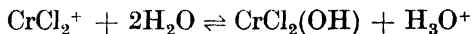


FIG. 101.—HYDROLYSIS OF SALTS AND MULTIVALENT IONS.

at the different concentrations taken, account may be taken of the effect. In calculating the concentrations of hydron arising from the degrees of hydrolysis of salts which undergo hydrolysis by stages, however, it has to be assumed that no superposition of the different equilibria for each stage occurs, so that each stage of hydrolysis is sharply marked off from the next. Moreover it often happens that the equilibria are disturbed by the separation of basic hydroxides in the form of suspensions and colloidal solutions, and these difficulties, which are inherent in the phenomena themselves, cannot be surmounted.

Interesting results were obtained by this method for the blue form of chromic chloride and for aluminium chloride and sulphate, where it was found that the degree of hydrolysis varied as a continuous function of the concentration as

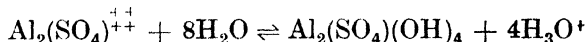
shown in the curves (Fig. 101). From the results so obtained, by substitution in the values for the equilibrium constants assuming first-stage hydrolysis (K_1), then second-stage hydrolysis (K_2), it was shown that in all cases, only the values of K_1 showed any degree of constancy, and that therefore the main reactions taking place during hydrolysis were probably :



and



In the case of aluminium sulphate, however, it was evident that the hydrolysis



was becoming increasingly important in dilute solutions.

Similar investigations on cobalt, zinc, and magnesium salts showed that the E.M.F. never remained steady, but that the hydron concentration varied irregularly from day to day. These anomalies were attributed to the possibility of hydrolysis leading to a heterogeneous system in which basic salts and hydrates might be present in colloidal suspension. In the case of ammonium chloride, the electrode potential was found to decrease with time due to loss of ammonia, but this could be eliminated by passing the hydrogen used at the hydrogen electrode through a series of wash-bottles containing ammonium chloride solution of the same concentration as that being measured, before it entered the electrode vessel. The measured potential was then found to fall to a minimum, followed by a slight rise to a steady value. The initial fall was attributed to the absorption of ammonia from the liquid around the electrode by the platinum, although hydrogen is absorbed much more rapidly. The subsequent slight rise was supposed to be due to an increase in the hydron concentration. The minimum value as measured by a number of independent experiments was therefore taken as giving the true potential. The degrees of hydrolysis at different concentrations were then found to be very small indeed—of the order of 0.005% at moderate dilutions.

CHAPTER XIV

NEUTRALISATION AND THE THEORY OF INDICATORS

SUBSTANCES like litmus and red cabbage have been used for a very long time for detecting acids and bases, and in recent years many new dyestuffs have been employed as acid-base indicators. Most of the substances in common use are definite compounds or, like litmus, contain some coloured active constituent ¹ which undergoes a suitable colour change from acid to alkaline media. The more common of these, which have proved most valuable by long-established usage for detecting the neutralisation of a basic by an acidic solution, are methyl red, congo red, methyl orange, and phenolphthalein. More recently, phenolphthalein has been replaced by *p*-nitrobenzene azo- α -naphtholsulphonic acid, which changes from yellow in acid to purple in alkaline solution, and has the advantage that an excess of alkali does not convert it into a colourless compound, as with phenolphthalein. A reference to the literature of industrial and analytical chemistry will reveal the enormous number of specific indicators which have been evolved for one purpose or another, and there is nothing to be gained by multiplying examples of these for the purpose of theoretical discussion. Mention should, however, be made of the "universal" indicators, such as those prepared by the British Drug Houses (the colour changes of which are given on p. 446), which undergo wide variations in colour, enabling them to be used over the whole range of hydrogen-ion concentrations encountered in ordinary work.

¹ For litmus, the coloured substance responsible for its indicator properties is azolitmin.

Ostwald's Theory of Indicators.

Ostwald ¹ applied the Arrhenius theory of ionic dissociation to the problem of indicator colour changes by supposing all indicators to be weak bases or weak acids. The colour of the indicator differed according as it was dissociated or not, the colour being attributed to the complex ion of the dissociated substance. Thus, Ostwald supposed that in neutral and acid solutions phenolphthalein, which is a weak acid, existed almost entirely in the undissociated form by the common ion

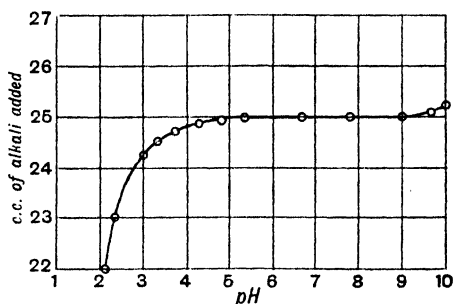
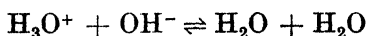


FIG. 102.—THE TITRATION CURVE FOR STRONG ACIDS AGAINST STRONG BASE.

effect (see p. 381), and was therefore colourless, but that on adding alkali, as soon as any excess of this was present, a salt of the weak acid phenolphthalein HP was formed, and, being highly dissociated, this salt gave rise to the coloured P^- ions. During the neutralisation of say 25 c.c.s of $N/10$ hydrochloric acid with $N/10$ caustic soda, the change in the hydrogen-ion concentration of the solution during the addition of the sodium hydroxide may be worked out if it is assumed that at these concentrations the hydrochloric acid is completely dissociated.² For, during neutralisation, the concentration of the hydrogen ions will decrease due to the ionic reaction:



¹ A review of earlier work on the theory of indicators is given by R. B. Bourdillon in *Trans. Oxford Jun. Sci. Club*, 1913.

² During the discussion of the Ostwald theory of indicators, the Arrhenius theory of ionic dissociation is of course assumed to account for the behaviour of solutions of electrolytes.

for which the equilibrium lies far over on the right-hand side, and the following simple calculations give the pH values at various stages of the reaction :

TABLE XIX.

Titration of 25 c.c. N/10 HCl with N/10 NaOH.

No. of c.c.s alkali added.	Total volume.	Total conc. of hydron present in the solution.	$pH = -\log_{10} (H^+).$
0	25	$\frac{N}{10} \frac{25}{25} = N \frac{1}{10}$	$-\log_{10} \frac{1}{10} = 1$
1	26	$\frac{N}{10} \frac{24}{26} = 0.0923N$	
2	27	$\frac{N}{10} \frac{23}{27} = 0.0852N$	1.065
23	48	$\frac{N}{10} \frac{2}{48}$	2.38
24	49	$\frac{N}{10} \frac{1}{49}$	2.69
24.5	49.5	$\frac{N}{10} \frac{1}{49.5} \frac{1}{2}$	3.00
24.95	49.95	$\frac{N}{10} \frac{1}{49.95} \frac{1}{20}$	4.50
25.0	50.0	$N \times 10^{-7}$ [as in water]	7
25.05	50.05	$\frac{N}{10} \cdot \frac{1}{50.05} \cdot \frac{1}{20}$	$\begin{cases} pOH \simeq 4.5 \\ pH \simeq 14 - 4.5 = 9.5 \end{cases}$

If the results exhibited in Table XIX are plotted graphically (Fig. 102) to show the pH of the solution against the number of c.c.s added, it is seen that in the region of the neutralisation point the pH of the solution changes very rapidly, and the addition of the slightest excess of alkali in this region causes an enormous difference in the pH . It is, of course, over this range that the indicator changes colour. The general shape of the titration curve may also be deduced theoretically, as follows. With equivalent solutions of acid and alkali each at a molecular concentration c , when v c.c.s of alkali have been added to V c.c.s of acid, the total volume of the solution is $(V + v)$. Assuming now, that there is

¹ Here the fraction $\frac{1}{20}$ represents the concentration of the OH^- ions.

complete dissociation of the acid, the total hydron concentration is given by :

$$c_{\text{H}_3\text{O}^+} = (V - v)c \text{ gram-ions} \quad . \quad . \quad (665)$$

and
$$[\text{H}_3\text{O}^+] = \frac{(V - v)c}{V + v} \quad . \quad . \quad . \quad (666)$$

gram-ions per c.c.

Thus
$$p\text{H} = -\log_{10} [\text{H}_3\text{O}^+] = \log_{10} \frac{V - v}{c(V + v)} \quad . \quad . \quad (667)$$

This is a general expression for the $p\text{H}$ of any solution and the method used in calculating the values of the $p\text{H}$ during the neutralisation of $N/10$ hydrochloric acid with $N/10$ alkali was essentially similar to that employed above in the general case.

Differentiating (667) logarithmically, and remembering that V is constant, we have :

$$\frac{\partial(p\text{H})}{\partial v} = \frac{1}{2.303} \left[\frac{1}{V - v} - \frac{1}{V + v} + \frac{1}{c} \right] \quad . \quad . \quad (668)$$

so that $\partial(p\text{H})/\partial v$ is infinite when $v = V$ —i.e., when an equal volume of alkali has been added to the acid, there is a vertical point of inflection on the graph of the $p\text{H}$ plotted against the volume of alkali added (Fig. 103, $\alpha^* = 1$). This has involved the assumption that the Arrhenius degree of dissociation of the acid remains equal to unity. All acids, however, have a true degree of dissociation, which, in “strong” solutions, at least, is not equal to unity. In general, if α^* denote the “true degree of dissociation,” this will vary during the titration due to the varying salt effect. If, however, it is assumed that α^* denote the value of the true degree of dissociation of the acid at the dilution corresponding to the addition

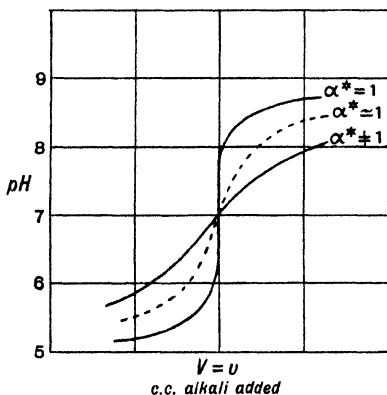


FIG. 103. CALCULATED TITRATION CURVES FOR VARIOUS VALUES OF α^* .

of v c.c.s of alkali, the value for the hydron concentration at this point of the titration will be :

$$[\text{H}_3\text{O}^+] = \frac{(\alpha^*c)(V-v)}{(V+v)} \quad . \quad . \quad . \quad (669)$$

from which

$$\frac{\partial(\text{pH})}{\partial v} = \frac{1}{2.303} \left[\frac{1}{c} - \frac{1}{V+v} + \frac{1}{V-v} \right] \quad (670)$$

as before. The slope of the $\text{pH} : v$ curve when $V = v$ is therefore the same no matter what the value of α^* is. Equation (670) predicts, indeed, that the whole curve has the same shape for any acid, but this is not actually the case, since we have assumed that α^* is independent of v , which it certainly is not. The general shape of the curve for (669) obtained when α^* is well removed from unity, in solutions of moderate dilutions—*e.g.*, for the titration of a weak acid with a strong base—is, however, shown in Fig. 103.

Ostwald derived a relation between the hydrogen-ion concentration and the degree of dissociation of the indicator, as follows. For a weak acid of dissociation constant K_1 , we have :

$$K_1[\text{HA}] = [\text{H}_3\text{O}^+][\text{A}^-] \quad . \quad . \quad . \quad (671)$$

and if α is the fraction ionised :

$$\alpha = \frac{[\text{A}^-]}{[\text{HA}] + [\text{A}^-]} \quad . \quad . \quad . \quad (672)$$

Substituting for the term $[\text{HA}]$ from (671), we have

$$\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{K_1} = \frac{[\text{A}^-]}{\alpha} - [\text{A}^-] \quad . \quad . \quad . \quad (673)$$

$$\text{i.e.,} \quad \log_{10} \left[\frac{1-\alpha}{\alpha} \right] = \text{pK} - \text{pH}^1 \quad . \quad . \quad (674)$$

The degree of dissociation of the indicator, and therefore, according to Ostwald, the intensity of its colour, thus appears to depend only on the hydron concentration. If for example $(\text{H}_3\text{O}^+) > 10K_1$, then from (674)

$$\frac{1-\alpha}{\alpha} > 10 \text{ and } \alpha < \frac{1}{11} \quad . \quad . \quad . \quad (675)$$

¹ The expression pK for an indicator is called the dissociation exponent and is given by

$$\text{pK} = -\log_{10} K_{\text{dis.}}$$

i.e., the indicator would be only about 9.1% dissociated, and so practically colourless. But if $(\text{H}_3\text{O}^+) < K_1/10$, α would be greater than $\frac{1}{11}$, and the indicator would then be more than about 91% dissociated and highly coloured to a corresponding extent. In the titration of hydrochloric acid by alkali, using rosolic acid as indicator, for which K_1 is approximately equal to 10^{-8} , there is, according to Ostwald's theory, practically no colour change when the $p\text{H}$ of the solution is 5, and the indicator will be only 9% dissociated when the $p\text{H}$ rises to 6. But when the $p\text{H}$ is 7, 91% of the indicator is dissociated, and consequently its colour has changed by then from red to yellow. The amount of alkali needed to reduce the hydrion concentration from 10^{-6} to 10^{-9} is, in the titration considered above, about 0.011 c.c., so that $\frac{1}{100}$ th. c.c. of alkali suffices to produce the whole of the visible colour change of the indicator. An indicator will therefore be sensitive to colour change over a specific range of $p\text{H}$ during titration, the range depending on its pK value.

In the case of the titration of a weak acid such as acetic acid with a strong base, the dissociation equation is (for acetic acid) :

$$K_{\text{acid}} = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\cdot\text{COO}^-]}{[\text{CH}_3\cdot\text{COOH}]} = 1.8 \times 10^{-5} . \quad (676)$$

When the $p\text{H}$ of the solution is 5, therefore :

$$1.8 \times 10^{-5} \times \frac{[\text{CH}_3\cdot\text{COOH}]}{[\text{CH}_3\cdot\text{COO}^-]} = 10^{-5} . \quad (677)$$

and if α_{acid} is the fraction of acetic acid which is undissociated :

$$\frac{\alpha_{\text{acid}}}{1 - \alpha_{\text{acid}}} = \frac{1}{18} . \quad (678)$$

or

$$\alpha_{\text{acid}} = \frac{1}{19} . \quad (679)$$

Similarly, when the hydrion concentration of the solution is given by $p\text{H} = 6$,

$$\alpha_{\text{acid}} = \frac{1}{19} . \quad (680)$$

In order to raise the $p\text{H}$ of the solution from 5 to 6, therefore, enough alkali must be added to neutralise an amount of acetic acid equal to $\frac{1}{14} - \frac{1}{19}$ of the original amount (say, 50 c.c.)—*i.e.*, 15.2 c.c. of alkali must be added. Methyl

red is orange at a pH of 5, and does not become yellow until the pH rises to a little above 6. If methyl red is used as indicator in this titration, 15.2 c.c. of alkali will have to be added in order to bring about the colour change, and it is evident, therefore, that methyl red is quite useless in such a titration. With an indicator like phenolphthalein, however, the change in colour begins at $pH = 8$ to 9. At this point in the pH range, all except about one two thousandth

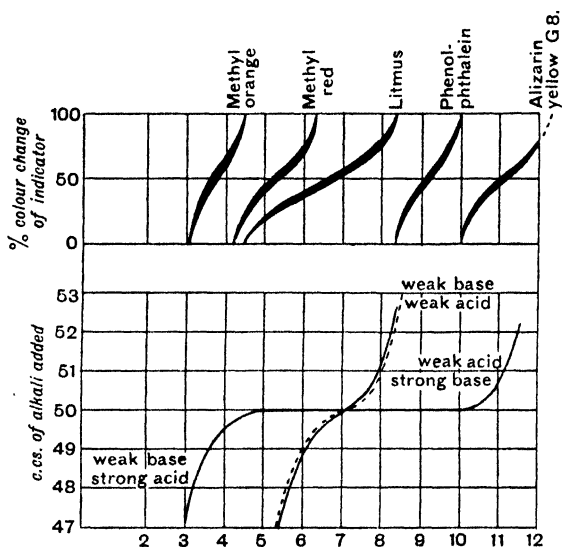


FIG. 104.—TITRATION CURVES, SHOWING INDICATOR RANGES.

part of the acetic acid has been neutralised, and the addition of one drop containing only 0.05 c.c. of alkali is more than sufficient to neutralise the remainder of the acid and bring about the colour change.

For the titration of a weak base by a strong acid, or a strong base by a weak acid, the buffering effect of the salt on the acid and the base suppresses their dissociations and the titration curves will have the form shown in Fig. 104. The exact value of the pH for any amount of alkali added to the acid may be found from the Henderson-Hasselbalch equation (see p. 451). The range over which the different

indicators are effective may be plotted as pH against the percentage colour change, the rate of change of the colour being marked by the thickness of the line. The range of pH , over which any indicator curve is thickest will then be that for which the particular indicator is most efficient, and it is therefore possible immediately to select the most efficient indicator for a particular titration. Titration curves may also be plotted from potentiometric measurements made during the titration, with the titrated liquid forming the half-cell solution of a hydrogen electrode connected with a standard calomel electrode. This method gives directly, and very conveniently, a measure of the change of pH as the alkali is added.¹ The pH at which the indicator is half dissociated is called the titration exponent pT , and a direct comparison of the pT of an indicator with the mid- pH of the range over which the titration liquid is neutral, will show immediately whether or not that indicator is suitable for the titration. The pH changes during the titration of a weak acid by a weak base show buffering effects on both sides of the neutral point, so that for pH 's less than that for the neutral point the curve will follow the weak acid-strong base curve, whilst above this pH range the behaviour observed for a weak base and a strong acid will be simulated. It is therefore evident that in such titrations, the solution will be subject to rapid pH fluctuations at all points of the titration, and great difficulty will be found in finding a suitable indicator, the pT value of which is sufficiently close to 7 to make the titration practicable. In laboratory practice, however, it is always possible to avoid the titration of a weak acid with a weak base by using a strong base for titrating a weak acid and a strong acid for titrating a weak base.

The titration of polybasic acids which have two or more separate dissociation constants one for each stage, will follow a curve formed by the superposition of two or more curves plotted for each dissociation constant separately, for any subsequent dissociation stage does not usually begin to be appreciable until the preceding dissociation is almost

¹ See Kohlthoff's "Colorimetric and Potentiometric Determination of pH " (Chapman and Hall); Kohlthoff and Furman, "Potentiometric Titrations" (Wiley).

complete (see Fig. 99). It is therefore possible, by the choice of suitable indicators, to titrate each stage separately, as if the acid did dissociate as three separate acids. The dissociation of one stage is never, however, quite complete before the next stage sets in (see p. 316), and the whole titration curve for one stage may therefore show a small buffering effect before the subsequent stage of dissociation predominates in the titration curve. Thus in the curve illustrated in Fig. 105 for the titration of 50 c.c. of $M/20$ phosphoric

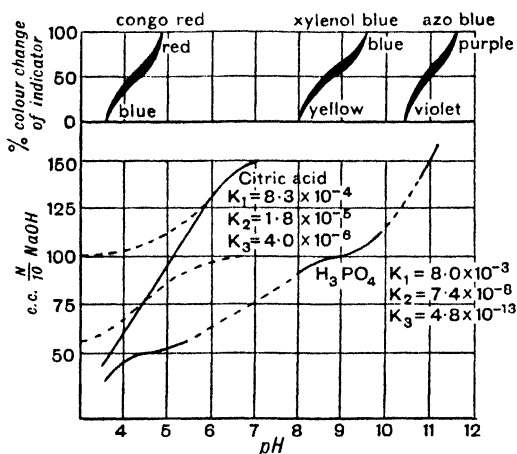


FIG. 105.—TITRATION CURVE FOR TRIBASIC ACIDS.

acid with $N/10$ potash, although the successive pK_{acid} values in this case are not sufficiently close together to obscure the effect, they are in a similar titration using citric acid. Here again the colour change curves of suitable indicators are shown, so that the way in which each separate dissociation may be titrated is illustrated. (The ordinate scale is made out of proportion between the successive 50-c.c. amounts of alkali added in order to keep the diagram within a convenient size.) The broken curved lines in the citric acid graph show the idealised curves which would be obtained by supposing that each stage of dissociation went to completion before the next stage of dissociation set in. It will be seen, however, that, due to the sharpness with which the curve rises at the 150-c.c. stage,

even with the indicator quoted, it will be almost impossible to attain an accurate end-point. Here the buffering effects on both sides of the true end-point are so considerable that the neutralisation process simulates the behaviour of a weak acid with a weak base, for here, too, the rate of change of pH as the alkali is added is so small as to make the choice of a single indicator almost impossible. It is, however, sometimes possible in cases like this, and in the titration of some weak acids with weak bases, to obtain a fairly accurate end-point even when no single indicator suitable for the pH range can be obtained, by using a universal indicator which undergoes a whole series of colour changes within a range of pH values.

As a general rule, the hydrion concentration at the end-point should never exceed one thousandth of the value of the dissociation constant of the acid being titrated. A satisfactory end-point requires at least a 100% colour change in the indicator (as measured by its degree of dissociation) which requires a 100% change in pH . A drop of alkali added at the end-point must therefore contain at least as high an OH^- concentration as that which already exists in the solution. One drop of tenth normal strong alkali (completely dissociated) contains $0.05 \times 0.001 \times 0.1 = 5 \times 10^{-6}$ gram-ions of hydroxyl ions (assuming one drop to be 0.05 c.c.), and if the titration is carried out with 50 c.c. of tenth normal acid, the hydroxyl-ion concentration at the end-point must not exceed $5 \times 10^{-6} \times \frac{1000}{50} = 5 \times 10^{-5}$ gram-ions per litre—i.e., the hydrion concentration must exceed 2×10^{-10} gram-ions per litre. It is not possible therefore to titrate accurately and to obtain a sharp end-point, with any acid, the dissociation constant of which is less than 2×10^{-10} . When it is necessary to carry out titrations with great accuracy in weak acids or weak bases using indicators, a standard solution is prepared containing a known volume of indicator solution, and this same volume of indicator is added to the titrated liquid, the end-point being observed at which the colour of the titrated liquid is the same as that of the standard. Such a standard may be prepared by neutralising a solution of the weak acid or base estimated gravimetrically, with

exactly one equivalent of hydrochloric acid or caustic soda, the solutions being of approximately the same strength as the titration liquids, so that the final volume will be the same in all cases. To this is added a measured quantity of the indicator solution, sufficient to produce a marked tint, and the resulting solution is used as the standard. Alternatively, a solution of the hydrochloride of the weak base or the sodium salt of the weak acid may be made up to approximately the same strength and volume as the titration liquids, and the indicator then added. Such standards do not maintain their colour for long without changing, and fresh standards have to be prepared for each new set of titrations.¹

The Structures of Indicators (Hantzsch's Theory).

Although Ostwald's theory of indicators, which assumes the colour changes to be produced merely by ionisation, appears to give a satisfactory explanation in terms of the Arrhenius theory of the observed facts which we have so far considered, there are nevertheless certain facts relating to the behaviour of indicators for which it does not give an adequate account. The solid salts of many of these indicators—*e.g.*, of methyl orange—which according to Ostwald are undissociated, are strongly coloured, so that the combination of the ions to form an undissociated solid indicator acid cannot explain the persistence of colour. Again, the addition of phenolphthalein to strong solutions of caustic soda produces no colour, and the supposed formation of a sodium salt of the indicator acid cannot explain this, since the sodium salt is itself red. The addition of acid to such a strongly alkaline colourless solution of phenolphthalein gives a red coloration only on heating. The methyl ester of phenolphthalein when it was first prepared was also found to be highly coloured, although esterification was supposed to reduce ionisation. Moreover, the colour becomes more intense when the ester is brought into acid solutions. These facts, which are inexplicable by Ostwald's theory, have, however, been

¹ Clark, "Determination of Hydrogen Ions," Baltimore, 1929.

satisfactorily accounted for by what we may call the "structural theory" of indicators. All the indicators which have been used for titrations of the acid-base type are organic substances, which, according to the theory of colour production due to Witt and others, can undergo tautomeric changes to give a chromogenic grouping (usually for these substances, a quinoid group) which has to be present before the substances show any colour,¹ together with a latent auxochromic or colour-strengthening group, necessary for the full development of the colour. The exact function of the auxochromic group is probably to introduce the possibility of resonance, the colour being ascribed to the intimate association of the chromophore with this resonance in the structure.² Such resonance in highly coloured compounds has been observed in certain cases by measurements of the change in the dipole moment,³ and, moreover, as there are almost certainly more possibilities of resonance in the solid state between adjacent molecules suitably disposed in the lattice, than between the different parts of the same molecule in solution, this view will explain the fact that many substances—as, for example, rosolic acid and quinhydrone—are intensely coloured only in the solid state, while being practically colourless in neutral solution.

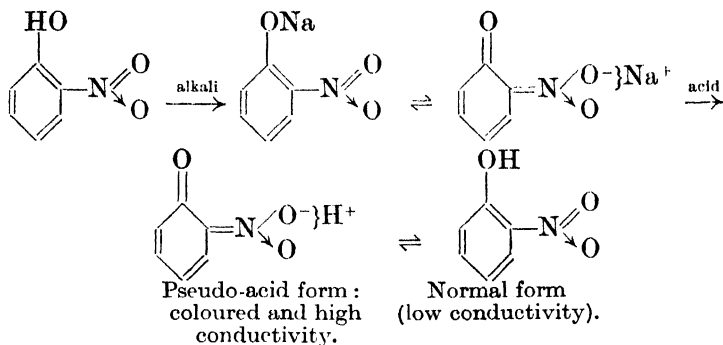
Hantzsch proved conclusively that a change in structure accompanies colour formation in the indicator type of compound, from conductivity measurements made on the yellow form of *para*-nitrophenol. By the action of alkalis on this, a salt could be obtained having a high conductivity, and when this salt was treated with a sufficient quantity of acid to reform the whole of the nitrophenol, the newly formed compound was found to have a deeper colour than the initial compound, and its colour was found gradually to fade to the original light yellow at the same time as the conductivity of the solution decreased.⁴ The series of changes supposed to take place was therefore represented by the following formulæ :

¹ Witt, *Ber.*, **9** (1876), 522.

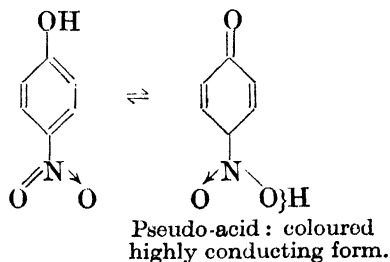
² C. R. Bury, *J. Amer. Chem. Soc.*, **57** (1935), 245.

³ Sutton, *Trans. Faraday Soc.*, **30** (1934), 789.

⁴ Hantzsch, *Ber.*, **39** (1906), 1091.



Further confirmation of the view that a deepening of colour takes place by pseudo-acid formation was provided by the isolation, by alkylation of the dry silver salt, of deeply red coloured *ortho* and *para* ethers, which were unstable, passing into the yellow form, and which had many of the properties of anisole. The formation of a pseudo-acid would not be expected, however, for *meta*-nitrophenol, and, in accordance with this, no ether could be obtained by alkylation of the silver salt of *meta*-nitrophenol. The ease with which the tautomeric change takes place in the *ortho*- and *para*-compounds is in agreement with other work on electromeric changes in benzene-substituted compounds, and the work of Baker confirms the formulation of the normal form of the *ortho*-nitrophenol with a double bond between the two groups, so that chelation can take place.¹ In the *para*-compound the tautomeric change is from :

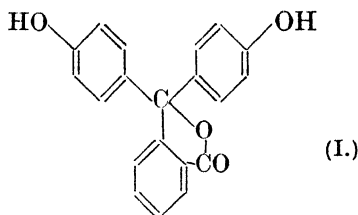


In both *ortho* and *para*-nitrophenols, therefore, the coloured

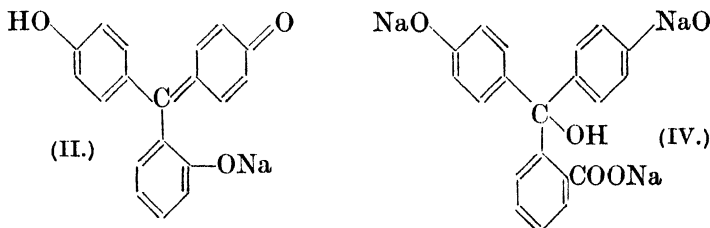
¹ Wilson Baker, *J.C.S.* (1934), 1, 648.

form has, according to Hantzsch, a quinonoid structure, and in the case of a *meta*-nitrophenol, where no *meta*-quinonoid form is known, the changes taking place in the other two compounds are absent. Hantzsch extended his experiments to other similar compounds, and showed that in all cases like changes occurred, and that the compounds could all be used as indicators for titrations of an acid against a base.

Stieglitz pointed out that similar structural changes, too, would explain the observed colour changes in phenolphthalein. The substance itself in the undissociated form has the structure (I) which does not contain any chromogenic grouping and which is therefore uncoloured.¹ In the presence of alkalis, however, the salt of the tautomeric quinonoid form (II) is produced and this has a bright red colour.



Green and Perkin's observation that, on adding a large excess of alkali, the red salt first formed became colourless,² was explained by Hantzsch, who supposed that a trisodium salt (III) was formed which, like phenolphthalein, would not

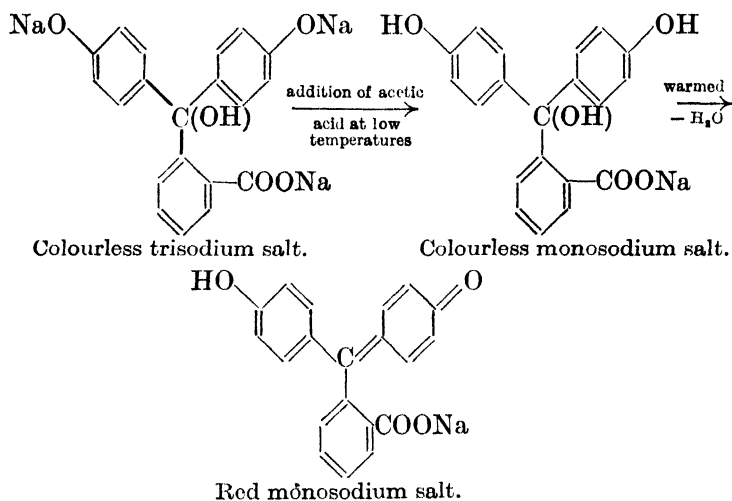


contain a chromogenic grouping, and which would therefore be colourless. Neutralisation of the strongly alkaline

¹ Stieglitz, *J. Amer. Chem. Soc.*, **25** (1903), 1112.

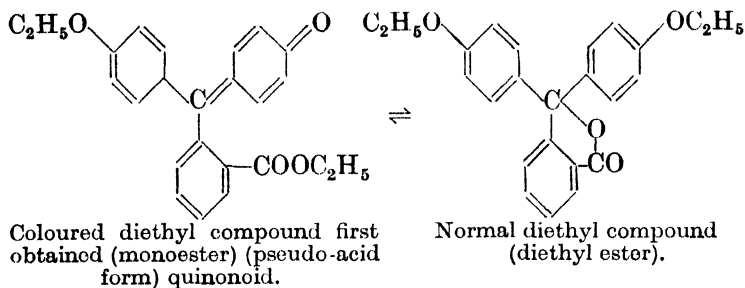
² Green and A. G. Perkin, *J.C.S.* (1904), 398.

solution with acetic acid at low temperatures did not result in the development of colour, but this reappeared on warming.¹ The addition of the acid was supposed to give the dihydroxy-compound from the trisodium salt which lost water only on warming, to give the red monosodium compound :



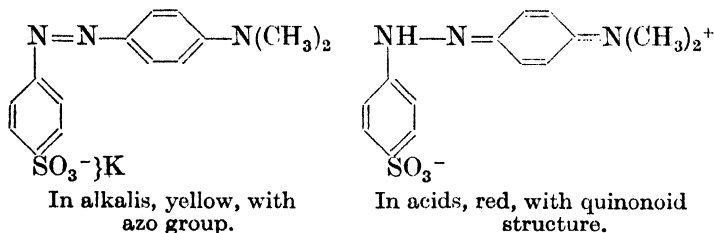
The fact that some of the colour changes require a measurable time for completion is strong evidence against the ionic explanation of indicator changes, for, according to the latter, all the reactions should be practically instantaneous. Sodium hydroxide in excess added to tetrabromophenolphthalein gives a solution of high conductivity, the value of the conductivity decreasing, however, on standing. This represents, therefore, exactly the behaviour of a pseudo-acid. The direct proof of the Hantzsch theory of the indicator action of phenolphthalein is due to Meyer and Merx, who showed that the silver salt of phenolphthalein, when treated with ethyl iodide, gives a coloured labile diethyl ester which passes slowly into a perfectly colourless substance isomeric with it. This proves conclusively that phenolphthalein can exist in two inter-convertible tautomeric forms, only one of which has the pseudo-acid quinonoid form.

¹ Green and King, *Ber.* (1907), 3724.



Hantzsch's theory of colour, as applied to the case of phenolphthalein, has received considerable support from the evidence for the structure of fluorescein derivatives.¹ Fluorescein is a phthalein derivative obtained by using resorcinol in place of the phenol used for phthalein, and an investigation of its esters and ethers shows that coloured compounds are obtained only where there is the possibility of a quinonoid structure being produced in the molecule. Colour, in this series, therefore, must be associated with the presence of a quinonoid grouping, and of course phenolphthalein is one member of the series.

An exactly similar explanation may be applied to all indicators used in acid-base titrations.² Thus in the case of an azo-dye such as methyl orange (which is obtained by coupling diazotised sulphanilic acid with dimethylaniline), this indicator in alkaline solution forms a salt having an azo-chromogenic group associated with a yellow colour. When the pH is decreased, however, a hydrogen ion is taken on by the structure, giving a zwitterion with a quinonoid arrangement, which therefore has a red colour :



¹ Nietzki and Schröter, *Ber.*, **28** (1895), 44.

² Stieglitz, *J. Amer. Chem. Soc.*, **25** (1903), 1124.
Küster, *Z. anorg. Chem.*, **13** (1897), 135.

In the sulphonphthalein series (the behaviour of all the members of which is analogous to that of phenol red), a large number of tautomers are possible, and although all of these may possibly be formed under different conditions, which particular ones are present in a given solution can only be deduced by drawing analogies from the behaviour of other indicators. Mixtures of indicators may be used either to modify the colour or, more usually, to extend the range of pH applicable, as in the case of the B.D.H. universal indicator, which undergoes the colour changes given in Table XX.

TABLE XX.

Colour Changes of B.D.H. Universal Indicator.

pH	4.2	4.8	5.1	6.8	7.3	9.1	10.3	11.5
colour	red	yellowish-red	orange-yellow	yellow	sap-green	greenish-blue	violet	reddish-violet

Although all acid-base indicators undergo changes in structure of the types outlined in a few special cases, above, not all substances showing these particular tautomeric properties together with a sufficient contrast of colour in the various forms are suitable as indicators. Some of the tautomeric changes—as for example with nitromethane—may be so slow that they render the substance useless as an indicator. Alternatively, the tautomeric change may take place over a range of pH unsuitable for acid-base titrations. For substances capable of being used as indicators, all the properties in relation to their behaviour in solutions of varying pH may, however, be explained by their tautomeric changes without making Ostwald's equivocal assumptions about the relation of colour intensity to the degree of dissociation. The range of applicability of an indicator, in pH values, is in fact that over which the tautomeric changes appropriate to the indicator take place, but not, as Ostwald supposed, the range over which simple dissociation would take place. Noyes has shown how the theory of ionic dissociation, which is valid for weak electrolytes, is modified

for the case of the tautomeric change in an indicator.¹ For, if the indicator exists in two tautomeric forms HT_1 and HT_2 , both of which ionise, three equilibria will be set up, two for the ionisation of the tautomers and one for the equilibrium between the tautomers. For the ionisation of the tautomer HT_1 :

$$\frac{(T_1^-)(H_3O^+)}{(HT_1)} = K_{HT_1} \quad . \quad . \quad . \quad (680)$$

For the ionisation of the tautomer HT_2 :

$$\frac{(T_2^-)(H_3O^+)}{(HT_2)} = K_{HT_2} \quad . \quad . \quad . \quad (681)$$

and for the equilibrium between the tautomers:

$$\frac{(HT_2)}{(HT_1)} = K_T \quad . \quad . \quad . \quad (683)$$

From these equations, it may be shown that:

$$\begin{aligned} \frac{(H_3O^+)[(T_1^-) + (T_2^-)]}{(HT_1) + (HT_2)} &= \frac{(T^-)(H_3O^+)}{(HT)} \text{ say} \\ &= \frac{K_{HT_1} + K_{HT_2} K_T}{1 + K_T} = K \quad (684) \end{aligned}$$

This reduces to an equation of the Ostwald form (674) if the sum $(T_1^-) + (T_2^-)$ is practically equal, either to (T_1^-) , or (T_2^-) —i.e., if one or other of the tautomers is almost completely responsible for the colour. The fact that such dissociation equations do represent the observed colour changes remarkably well, appears to show that either K_T is very large or very small, so that in acid-base indicators one of the tautomers is almost exclusively responsible for the colour. The observed dissociation constant K is termed by Noyes the "apparent dissociation constant," and it is a function of the ionisation and equilibrium constants set up by the tautomers. As a means of formal representation, it is therefore very convenient to regard Ostwald's theory as having been modified only to this extent—that his $K_{\text{indicator}}$ is replaced by the Noyes "apparent dissociation constant," which depends on the tautomeric equilibria of the indicator in the

¹ A. A. Noyes, *J. Amer. Chem. Soc.*, **32** (1910), 815.

particular solution. The Ostwald theory did not, however, give a correct interpretation of the experimental data for indicator colour changes, for whereas it attributed colour change solely to dissociation of the indicator as a weak acid or a weak base, the more recent theory realises that the colour of the indicator is associated with a tautomeric form rather than with a simple ion, and that change in colour is due to the interaction of the ionisation equilibria of these tautomers with the tautomeric equilibrium itself. The Hantzsch theory of indicators differs from the Ostwald theory, in fact, in just so much as follows from the substitution of more complex tautomeric forms of the indicator, each associated with its particular colour, for the simple one-form indicator molecule.

Buffer Solutions.

The fact that different acid-base indicators change colour over a specific range of pH values has an important application in the estimation of hydron concentrations of solutions. This problem is of particular importance in biochemistry, for in life-processes the maintenance of a specific range of hydron concentration in solutions found in the animal or plant cells, may be of the utmost importance for the satisfactory operation of these processes. One of the difficulties which is encountered in trying to give an explanation of the fundamental transformations which are taking place in the living cell, by observations of varying physical conditions imposed upon it, is that the successful operation of the cell may depend upon the pH of the solutions remaining steady to within very narrow limits, and it is at present quite impossible to achieve anything approaching this degree of accuracy in the measurements of hydron concentrations. Of the methods available for the measurement of these important functions, one of the most important, especially in industrial problems, where it is only necessary to regulate the hydron concentration approximately, or where any rapid approximate determination is sufficient, is that which employs indicators of known pH ranges. Evidently, however, before it can be possible to apply this principle it is necessary to have some easy method of keeping a standard

solution at a definite known pH value, which will not be affected by absorption of carbon dioxide from the atmosphere, alkali from the glass vessels used, or any other soluble impurities which may be present. Such solutions of strongly resistant pH values are known as buffer solutions. Buffer effect is defined by van Slyke ¹ as the quantity given by the expression $\partial B/\partial(pH)$ or by

$$\frac{\partial A}{\partial(pH)} = - \frac{\partial B}{\partial(pH)}$$

B and A representing respectively the concentrations of strong base or acid added to the buffer. A unit buffer is therefore one, such that, to one litre of it, one gram-molecule of hydron or hydroxyl ion must be added in order to change its pH value by unity.

The value of $\partial B/\partial(pH)$ was obtained by van Slyke from the equation for the dissociation constant of an acid, which in its approximate form—*i.e.*, represented with concentration terms—and with the Arrhenius degree of dissociation α is

$$K_{\text{acid}} = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H_3O^+]\alpha}{1 - \alpha} \quad . \quad . \quad (685)$$

$$\text{i.e.} \quad \alpha = \frac{K_{\text{acid}}}{K_{\text{acid}} + [H_3O^+]} \quad . \quad . \quad . \quad (686)$$

Hence, by rearranging and taking logarithms,

$$pH = pK_{\text{acid}} + \log_{10} \frac{\alpha}{1 - \alpha} \quad . \quad . \quad . \quad (687)$$

By converting to natural logarithms and differentiating (687) we obtain the relation :

$$\frac{\partial \alpha}{\partial(pH)} = \frac{1}{e} \frac{\alpha}{1 - \alpha} \quad . \quad . \quad . \quad (688)$$

Also from the Henderson-Hasselbalch equation (695)

$$\begin{aligned} pH &= pK + \log \frac{[\text{Salt}]}{[\text{acid remaining}]} \\ &= pK_{\text{acid}} + \log \frac{[\text{base}]}{[\text{residual acid}]} \end{aligned} \quad (689)$$

¹ van Slyke, *J. Biol. Chem.*, 52 (1922), 525.

and comparing this with (687)

$$\alpha = \frac{[\text{base added}]}{[\text{total acid}]} \quad . \quad . \quad . \quad (690)$$

$$\text{i.e.} \quad \partial\alpha = \frac{\partial B}{[\text{total acid}]} \quad . \quad . \quad . \quad (691)$$

Thus from (691) and (688)

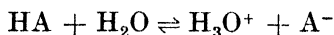
$$\frac{\partial B}{\partial(pH)} = 0.2303 \frac{\alpha}{1 - \alpha} [\text{total acid}] \quad . \quad . \quad (692)$$

In plotting the buffer index for any particular solution over a range of pH , however, account must be taken at high and low pH 's of the buffering effect of the strong base or acid then present, but this may be calculated by putting $\partial B = \partial(OH^-)$ on the high pH side or $\partial B = \partial(H_3O^+)$ on the low pH side—*i.e.*, by assuming that the strong acid or base is completely dissociated under these conditions.

The most efficient buffer solutions contain a weak acid together with its own salt, boric, phosphoric, or acetic acids being most commonly used. For pH solutions up to 7 and for pH 's from 7 to 10, solutions of sodium dihydrogen phosphate and hydrochloric acid are usually used, and from $pH = 10$ onwards, caustic soda replaces the hydrochloric acid. A universal buffer solution may be obtained by adding calculated quantities of caustic potash to a mixture of phosphoric acid (the three stages of dissociation operating), phenylacetic acid, and boric acid, or, alternatively, to a mixture of citric acid, phosphoric acid, barbitone, and boric acid.¹ Buffers from pH 's of about 2 to 12 (in the case of the second mixture quoted, a straight line buffer from 3.55 to 9.0) may therefore be prepared and used in the investigation of colour changes in universal indicators. In these solutions of mixtures of a weak acid or base, together with its own salt, the dissociation of the weak acid, always small, is repressed due to the common ion effect. Addition of a little hydrogen ion to such a solution causes this to associate with the anions from the salt, of which an excess is always available, to form the acid, and this process continues until the pH of the solution has returned to its initial value. The large excess of

¹ Prideaux and Ward, *J.C.S.*, 125 (1924), 456.

anions due to the presence of the salt, assures that the extent to which dissociation of the acid takes place shall be kept practically constant for small additions of hydrion. In the presence of hydroxyl ions, the hydrions and hydroxyl ions unite to form water, and more acid dissociates to replace the hydrogen ions used up. In each case it may be assumed that all the anions come from the salt, for the acid dissociation constant is only quite small, thus :



and $\text{MA} \longrightarrow \text{M}^+ + \text{A}^-$ (complete dissociation)

for which
$$K_{\text{acid}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad . \quad . \quad . \quad (693)$$

the term $[\text{H}_2\text{O}]$ being constant, *i.e.*, from (693):

$$[\text{H}_3\text{O}^+] = \frac{K_{\text{acid}}[\text{HA}]}{[\text{A}^-]} = \frac{K_{\text{acid}}[\text{HA}]}{[\text{MA}]} \quad . \quad (694)$$

$[\text{MA}]$ being the initial salt concentration

or
$$p\text{H} = pK_{\text{acid}} - \log_{10} \frac{[\text{acid}]}{[\text{salt}]} \quad . \quad . \quad (695)$$

This is the well-known Henderson-Hasselbalch equation, which allows a calculation of the $p\text{H}$ to be made in any solution containing an acid and one of its own salts. The problem is obviously one of the greatest importance in the preparation of buffer solutions.

As an example of the application of this equation, suppose it were required to know how many c.c.s of tenth normal acetic acid would have to be added to 1000 c.c.s of tenth normal sodium acetate solution in order to give a solution of $p\text{H} = 5$. From equation (695) we have :

$$5 = -\log_{10} (1.8 \times 10^{-5}) - \log \frac{[\text{acid in c.c.s}]}{1000} \quad (696)$$

expressing the total acid and salt concentrations as total volumes (which is equivalent to representing them on the same concentration scale, since they were taken in solutions of the same molar strength) *i.e.* :

$$\begin{aligned} \log [\text{acid}] - 3 &= -\log 1.8 \\ \log [\text{acid}] &= 2.7447 \quad . \quad . \quad . \quad (697) \end{aligned}$$

so that 555.5 c.c.s of acid would be required to give a solution of the requisite pH .

Although "complete" equations like the Henderson-Hasselbalch equation, which are based on the simple ionic theory, are obeyed for dilute solutions, they fail to reproduce the accurate E.M.F. measurements at higher concentrations (greater than tenth normal). Thus the simple equation predicts a constancy in the pH values over a range of dilutions, when the ratio of acid to salt is constant, but such constancy is not, in fact, observed. Cohn showed this failure of the simple ionic equation by plotting

$$pH = pK + \log \frac{[H_2PO_4^-]}{[HPO_4^-]} \quad . \quad . \quad (698)$$

for the same ratio of potassium dihydrogen phosphate and dipotassium hydrogen phosphate (obtained by adding the appropriate quantities of potassium hydroxide to the potassium dihydrogen phosphate solution) at different concentrations of the solutions. The value of pK was then found to vary from 6.188 to 6.856.¹ The Henderson-Hasselbalch equation (695) can, however, be corrected by employing activities in place of concentrations, so that for a phosphate buffer, (698) becomes

$$pH + \log \frac{(H_2PO_4^-)}{(HPO_4^-)} = pK' \quad . \quad . \quad (699)$$

pK' being now the corresponding expression in terms of activities.

$$\text{Also} \quad [H_2PO_4^-] = \frac{(H_2PO_4^-)}{f_{H_2PO_4^-}} \quad . \quad . \quad (700)$$

i.e.,

$$pH + \log \frac{[H_2PO_4^-]}{[HPO_4^-]} = pH + \log \frac{(H_2PO_4^-)}{(HPO_4^-)} + \log \frac{f_{H_2PO_4^-}}{f_{HPO_4^-}} \quad (701)$$

and from (698) and (699)

$$pH + \log \frac{[H_2PO_4^-]}{[HPO_4^-]} = pK' - \log \frac{f_{H_2PO_4^-}}{f_{HPO_4^-}} = pK \quad (702)$$

Using now the extended Debye-Hückel equation (320) to give the ratio of the activities, in which a term $D\mu$ is introduced to allow for the so-called "salting-out effect" in moderately

¹ Cohn, *J. Amer. Chem. Soc.*, **49** (1927), 173.

concentrated solutions, we have for the case of phosphoric acid :

$$-\log \frac{f_{\text{H}_2\text{PO}_4^-}}{f_{\text{HPO}_4^{2-}}} = \frac{0.5z_1z_2\sqrt{\mu}}{(1 + \alpha K)} - D\mu \quad (703)$$

and from (702) therefore :

$$\text{pH} + \log \frac{[\text{H}_2\text{PO}_4^-]}{[\text{HPO}_4^{2-}]} = \text{pK}' - \frac{0.5z_1z_2\sqrt{\mu}}{(1 + \alpha K)} + \frac{D}{\mu} = \text{pK} \quad (704)$$

In this equation D is a constant for various dilutions of the same mixture, provided the ratio of concentrations is unaltered, and its value in various cases has been found. Values of pK' may then be found from the observed hydrogen potentials which give 0.69×10^{-7} as the value of the second dissociation constant of phosphoric acid, and this remains constant over the range of concentrations employed for verifying equation (704) (up to 1.2M). Cohn's experimental data show that the equation does account, quite accurately, for the simple equilibrium equation if the mean ionic diameter is assumed to have a value 5×10^{-8} cm. The accuracy of the equation is for example very well illustrated from the plot of pK' against $\sqrt{\mu}$ shown in Figure 106, where the straight line represents the predictions of the simple equation. The corrected equation therefore enables solutions of any ionic strength to be made up to any desired pH , and the method has been extended to the acetate system for which the relevant equation is :

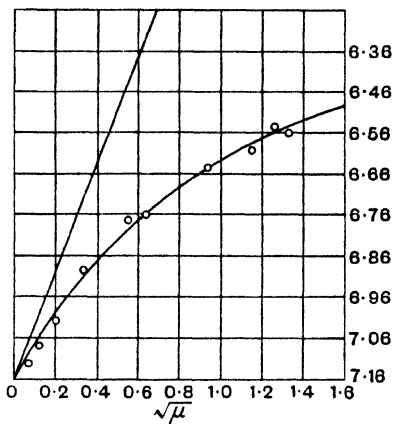


FIG. 106.—CORRECTION CURVE FOR pK' FOR A PHOSPHATE BUFFER (Cohn).

$$\text{pH} - \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \text{pK}' - \frac{0.5\sqrt{\mu}}{1 + \alpha K} + D\mu = \text{pK} \quad (705)$$

since in this case $z_1z_2 = 1$.¹

¹ Cohn, Heyroth, and Menkin, *J. Amer. Chem. Soc.*, 50 (1928), 696.

If a buffer solution is to be equally efficient towards acids and bases, the changes taking place when a small quantity of hydron is added must be exactly reversed by the addition of an equal quantity of hydroxyl ion—*i.e.*, $[HA]$ must be equal to $[A^-]$ or

$$[HA] = \alpha_{MA}^* [MA] \quad . \quad . \quad . \quad (706)$$

where α_{MA}^* is the true degree of dissociation of the salt MA at the particular concentration $[MA]$. Since also

$$[H_3O^+] = K_{acid} \frac{[HA]}{[A^-]} \quad . \quad . \quad . \quad (707)$$

it follows that, when the condition for equally efficient buffering is fulfilled :

$$pH = pK \quad . \quad . \quad . \quad (708)$$

If no acid is obtainable which fulfils this condition for the required pH of the solution, a buffer of this required pH may be made up by adding a sufficient quantity of salt in accordance with the condition below, when the buffer solution will be equally efficient in either direction. For if,

$$[H_3O^+]_n = K_{acid} \quad . \quad . \quad . \quad (709)$$

(709) becomes

$$[H_3O^+]_n = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H_3O^+]\alpha_{MA}^*[MA]}{[HA]} \quad (710)$$

$$i.e. \quad \frac{[HA]}{[MA]} = \frac{\alpha_{MA}^*}{n} \quad . \quad . \quad . \quad (711)$$

As there are two interdependent unknowns in the equation, it can only be solved by the method of successive approximations by choosing some value of α_{MA}^* , calculating $[MA]$ and substituting the new value of α_{MA}^* at this concentration—two or three of these processes will then give quite an accurate value for the ratio $[MA]/[HA]$.

Colorimetric Estimations of pH Values.

For very rough determinations of the pH 's of solutions, the use of buffer solutions may be avoided by employing a number of indicators the colour changes of which take place over overlapping ranges of pH . Thus, for a solution of pH

value 5, although both bromphenol-red and bromthymol-blue are yellow in colour, methyl-red is red and bromcresol is green, whereas at a pH 4.5, only methyl-red is red and all the others are yellow. In this way, therefore, the pH of a solution may be fixed between rather wide limits. A more accurate determination may be made once the approximate pH of the solution to be measured is known, by adding to the liquid to be measured an accurately measured quantity of indicator the pH range of which is recognised, from the approximate determination, to be suitable for use with the particular solution. The colour of a given depth of this solution contained in a cell having a carefully polished parallel plate bottom, is then compared with a similar depth of, say, a universal buffer solution containing the same volume of indicator in a similar cell. The value of the pH of the buffer may then be changed by adding varying quantities of alkali until the solution has, first a colour very slightly deeper than that of the unknown solution, then one very slightly lighter.¹

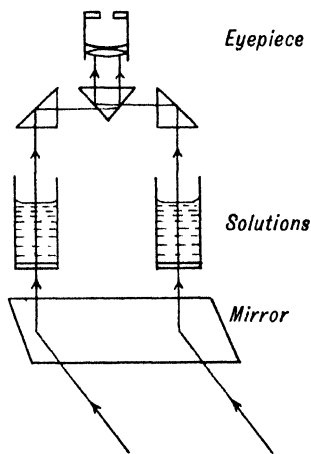


FIG. 107.—SIMPLE COMPARATOR.

The comparator itself is a device whereby the same transmitted light passes through both solutions and is reflected by prisms into the same eye-piece (Fig. 107), the prisms being covered on their long faces with a pattern such that the image from the light from one solution is alternate with that from the other. A better method, due to Gillespie, uses a modified compensating comparator² (see Fig. 108). In this the light is viewed directly from one cell containing the unknown liquid and a known volume of indicator. That which passes through the other has traversed two sections of liquid, one moving within the other. The moving

¹ See W. M. Clark "Determination of Hydrogen Ions" for a more complete account of this subject and for references.

² Gillespie, *J. Bact.*, 6, 199.

cell contains the same concentration of indicator taken to complete acidity, whilst the fixed cell is filled with indicator solution at the same concentration but taken to complete alkalinity. The unknown liquid in its cell, which moves with the acid indicator, is surrounded by distilled water to compensate approximately for the difference in intensity of the transmitted light which would otherwise be caused by the greater depth of the one side than the other. By moving the acid indicator up or down, so that a known depth of acid

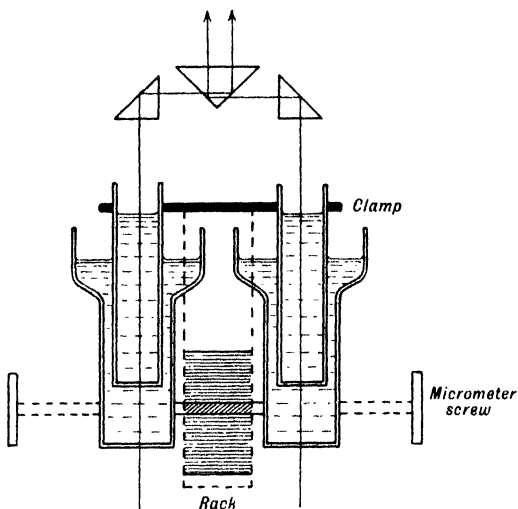


FIG. 108.—GILLESPIE'S COLOUR COMPARATOR.

indicator is viewed together with a measured depth of alkaline indicator, the tint of the indicator in the same concentration as in the unknown liquid may be imitated for any pH within the indicator's range. When the colours are the same in the field, therefore, the pH of the unknown liquid is equal to the imitated pH of the acid-alkaline indicator which is given by the equation

$$pH = pK + \log \frac{\text{colour due to alkaline solution}}{\text{colour due to acid solution}}$$

$$\text{or } pH = pK + \log \frac{\text{thickness I}}{\text{thickness II}} \cdot \cdot \cdot \cdot (712)$$

A similar device due to Bjerrum¹ is the so-called "colour wedge," which consists of a long tank having a plane plate bottom, but divided into two parts by an accurately fitting diagonal plate with parallel sides (Fig. 109). Into the compartment below this is placed a solution of the indicator at the same concentration as in the unknown solution, but coloured to complete alkalinity. By comparing the colour of the unknown solution with that of the liquid in the trough seen by transmitted light at various points along its length, the same result may be achieved as by the comparator method. This method of reproducing the colour of the indicator in solutions of varying pH , however, is considerably more bulky than the simpler method of Gillespie, and it



FIG. 109.—BJERRUM'S COLOUR WEDGE.

cannot be so easily incorporated into a comparator for direct comparison with the unknown solution. In all these apparatus the glass used must be such that it will not materially affect the pH of the solutions in the cells by the presence of any soluble impurity, and it is found that well-steamed-out Jena glass vessels serve the purpose well.

When the unknown solution is itself coloured, Walpole's method may be adopted. The known solutions are superposed over an equal depth of unknown solution as that contained in its cell, the same indicator being viewed as before through a thickness of distilled water equal to that of the known solutions and through the underlying unknown sample solution. In this way the light reaching both parts of the field observed will have passed through equal depths of the coloured sample solution.²

Although the use of indicators will give a rapid determination of the hydrion concentration of a solution, it is important

¹ Bjerrum "Die Theorie der Alkalimetrischen und Azidimetrischen Titrierungen," Stuttgart (1914), p. 31.

² Hurwitz, Meyer, and Ostenberg, *Proc. Soc. Exp. Biol. Med.*, **13**, 24. For other methods of determining pH values in solutions by indicator methods, see W. M. Clark, *op. cit.*, Chap. VI.

to realise that any such determination is only approximate, and for accurate determinations electromotive methods, employing the hydrogen or quinhydrone electrodes, must be used. There are, however, certain solutions, particularly those which may be encountered in connection with biological work, where the application of electrometric methods is severely restricted by the presence of foreign substances, present as colloids or as suspensions which can interfere with the equilibria at the interface between the solution and the electrode. In such cases determinations have to be carried out in homogeneous media by the use of indicators and buffer solutions, and it is chiefly in the field of biological work, therefore, that the colorimetric methods described above find their widest applications.

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